DESIGNING CROSSLINKED POLYMER NETWORKS AS ELECTROLYTES FOR LITHIUM BATTERIES

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By

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ABSTRACT

Lithium batteries are the dominant power source in portable device technology and are poised to play a similar, important role in electrified transportation systems. While significant strides have been made in recent years in evolving the cathode chemistry and electrolyte formulations to meet higher energy storage demands, almost all contemporary LIB designs rely on flammable electrolyte solvents that are fundamentally unsafe. In this thesis, we explore crosslinked polymer networks as safe electrolytes for Lithium based battery systems. We thoroughly investigate the ion conduction mechanisms in these networks and exploit their degrees of freedom to create multifunctional electrolytes.

We then report a facile UV cross-linking chemistry that can be used to create ion-conducting polymer networks containing dangling chains that impart specific, desired functionalities to liquid electrolytes. We show in particular that incorporation of monofunctional sulfonate and phosphate species in a photo-/heat-initiated cross-linking reaction of a multifunctional oligomer provides a straightforward route to mechanically robust membranes able to transform both transport properties and flammability of standard liquid electrolytes incorporated in their pores.

We evaluate the physical and mechanical properties of the materials and on that basis report that dangling functional groups in the membrane pores can improve electrolyte properties, without compromising performance in electrochemical cells. Such cross-

linked membranes with different pendant groups covalently tethered to an ion-conducting framework are argued to provide an important platform for more broadly enhancing lithium battery performance.

BIOGRAPHICAL SKETCH

Sanjuna Stalin was born in Tanjore, India and was brought up initially in Singapore and then Chennai, India. Her primary school teachers instigated interest in science and her father greatly inspired her to take up engineering as a major in her undergraduate institution, NIT, Trichy. Four years at NIT, Trichy was truly transformative for her, teaching her invaluable lessons about life away from home and the importance of good education. Her peers, mentors and especially her family motivated her to aim higher and were instrumental in securing an offer to pursue a master's degree at Cornell University with Prof. Lynden Archer.

Dedicated to my late grandfather, parents, and sister

ACKNOWLEDGMENTS

I would like to extend my sincere gratitude towards my advisor, Prof. Lynden Archer, who serves as a constant source of motivation as an enthusiastic researcher. His timely advice and exceptional guidance has made this journey smoother and easier than expected. I really look forward to working on more innovations and solving new research problems with you Professor! I would also like to thank my committee members Prof. Yong L. Joo and Prof. Christopher K. Ober for providing helpful insights before and during my defense.

When I first joined the Archer group, Prof. Archer directed me to Snehashis for training and guidance within the lab. I am immensely grateful to him for everything he has taught me, right from how to use the glovebox to fundamentals of conducting scientific research. His research aptitude, passion for teaching and humility will always be an inspiration for me and I am glad that he also became a very good friend over the past year. I will miss our deep conversations outside lab and I know you will do great wherever you go Sneh! My other lab mates and all my other friends at Cornell have made life within lab and Ithaca very pleasant and enjoyable.

I am truly blessed to have my parents and sister by my side during this journey. Staying away from home was not new, but overcoming many other hurdles was only possible because of them. I will forever be grateful to my father's immense generosity and high priority for my goals despite his own personal struggles. Thank you! Last but not least, I would like to thank Bala for being a pillar of support during tough times and for always being there no matter what.

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CHAPTER 1: INTRODUCTION

Lithium batteries

Lithium ion batteries have revolutionized the field of portable tools and consumer electronics due to their high volumetric and gravimetric energy densities. With growing demands for electrification of transportation and for reducing greenhouse emissions and use of the fossil fuels that produce them, focus on lithium-based battery technologies have increased over the past few years. Lithium batteries are also finding increasing applications in grid storage, where they provide storage that balances the effects of intrinsic intermittency of renewable electricity generation technologies such as solar and wind. Future urban designs are touted to provide fertile commercial opportunities that unify applications of batteries in transportation and grid storage. Energy, power, charge− discharge rate, cost, cycle life, safety, and environmental impact are some of the parameters that should be considered in adopting lithium ion batteries for various applications[1].

A lithium battery is composed of an anode, cathode, an ionically conducting but electrically insulating electrolyte and a separator that prevents contact between the two electrodes. The cell is connected to an external circuit, which enables electrical energy to be harnessed from chemical reactions at the electrodes during battery discharge and for electrical energy to be stored in the cell via electrochemical changes at the electrodes during charge. The chemistry of the electrode components therefore dictates the capacity and cell potential which in turn determines the energy density obtainable from the system.

Rechargeable lithium batteries come in two dominant forms, the Lithium-ion battery (LIB) and the Lithium metal battery (LMB).

Typical configurations of these two lithium battery designs are shown in Fig 1.1[2]. A key distinction is that whereas the LMB utilizes a metallic lithium foil as anode, the LIB uses a graphitic carbon material as the anode. This difference has many important consequences for battery operations, stability, and manufacturing. The most important is that whereas the LMB stores energy in the anode by reduction of Li-ions to the metal, in a LIB Li is stored in ionic form and the graphitic carbon host Li as LiC_6. As a consequence, the maximum/theoretical gravimetric anode storage capacity of an LMB is approximately 10-times larger (3860 mAh/g vs 360 mAh/g) than that of the LIB. An additional consequence is that recharge of a LMB requires electroplating of Li onto itself, a process that is unstable to formation of rough mossy and dendritic structures on the anode (see Fig. 1a), which introduce a variety of practical challenges some of which will be addressed later in this thesis.

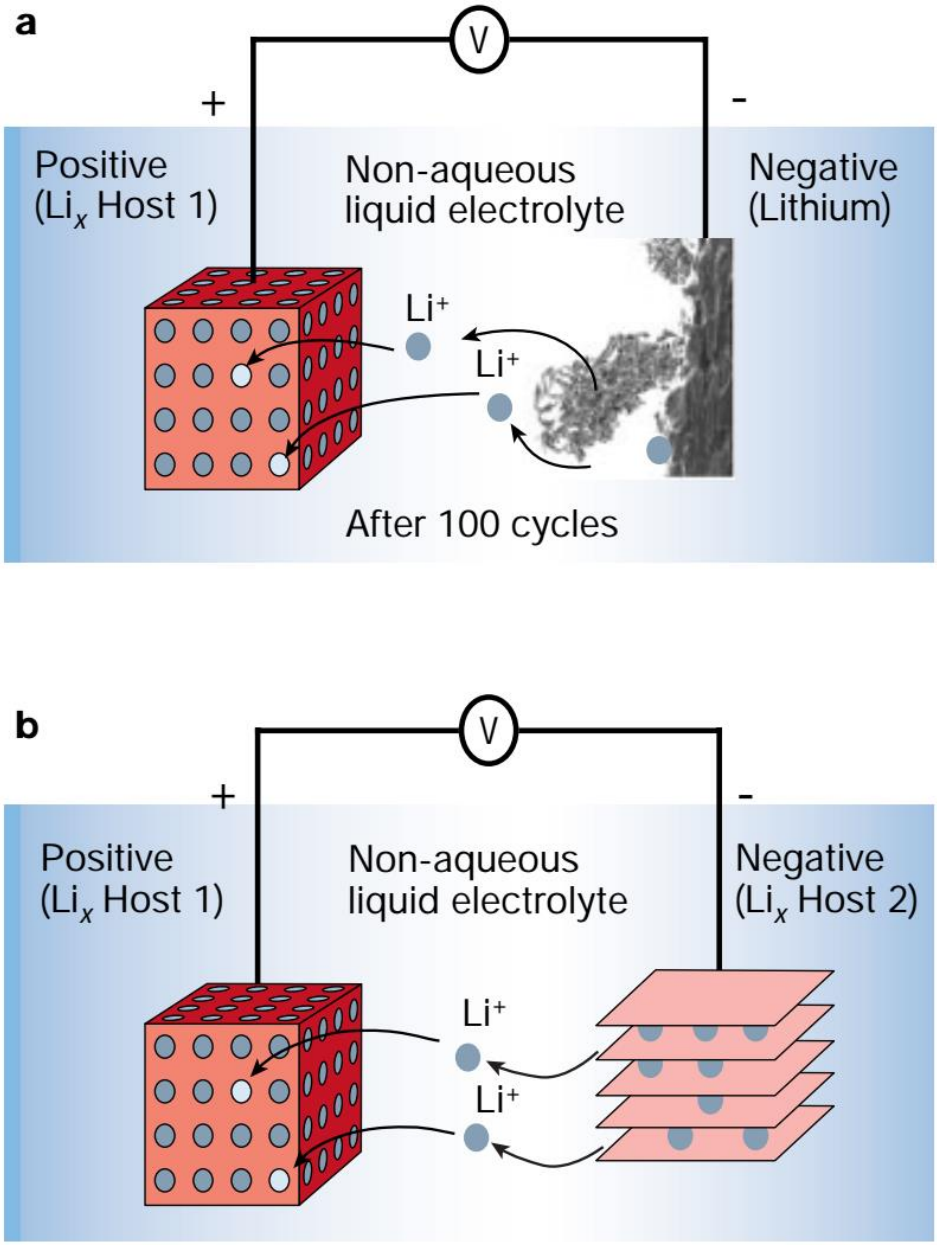

Fig 1.1: Schematic of a Lithium based battery setup. (a) A Lithium metal based electrochemical cell, with dendritic growth after 100 cycles, (b) A Lithium ion battery whereby Li^+ ions shuttle from one electrode to another[1]

A large number of cathode materials and electrolyte designs have been achieved over the past few years, which has brought the community a step closer to realizing the dream of complete elimination of fossil fuel dependence. An overview of these developments is presented in the following sections.

Electrode material developments

Fig 1.2 shows the volumetric and gravimetric energy densities of various battery technologies[2].

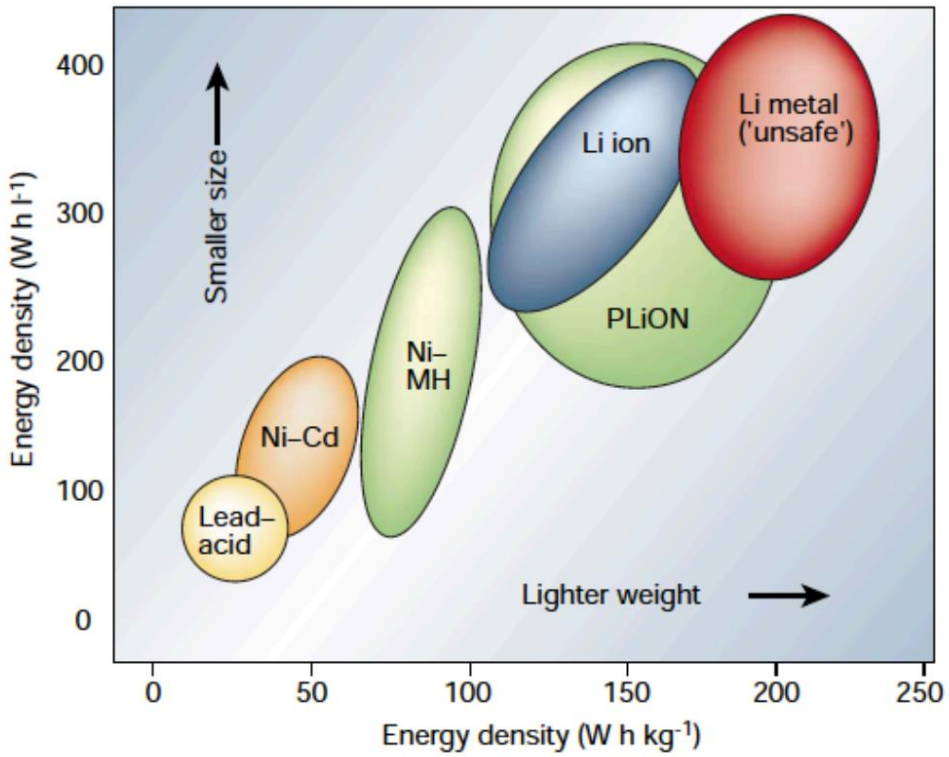

Fig 1.2 Volumetric and Gravimetric energy densities of different electrode chemistries and combinations[2]

It is evident that lithium-based batteries have the highest energy densities amongst all known systems, making them the most attractive choice for applications where size and weight matters. Intercalation compounds like LFP($LiFePO_4$), LCO ($LiCoO_2$) and NMC ($LiNiMnCoO_2$) are traditionally used as cathode materials in lithium batteries. The negative anode is a carbonaceous material like graphite in case of Lithium ion batteries. This system is also referred to as rocking chair technology, where the lithium ions insert and de-insert between the two intercalating electrodes. Lithium batteries with this design are regarded as inherently safer because the charge process neither produces metallic Li nor relies on electrodeposition of the metal. The cells nonetheless rely on volatile solvents to produce electrolytes with acceptable ionic conductivities and stability at the electrodes, which introduce other types of safety risks, particularly in abused batteries.

Growing demands for lithium batteries that offer higher power and energy densities required to compete with fossil fuel use in transportation have increasing interest in LMBs. Because of its much higher storage capacity, conceptual simplicity (the electrode is just a sheet of the metal that in principle requires no additional processing steps during battery manufacturing), and potential of a Li metal anode to paired with a large range of Lithiated and non-lithiated materials as cathodes, the lithium metal anode is considered the holy grail of next generation battery technology. Stanley Whittingham developed the world's first rechargeable lithium metal-based cell in 1972 in Exxon Research and Engineering company. He used a Titanium disulfide (TS_2) as the intercalating cathode, lithium metal as the anode and lithium perchlorate in dioxolane as the electrolyte. The main drawback of sulfides and chalcogenides as the intercalating cathode was that they had very low operating voltages (<2.5 V) vs lithium metal anode. This has been revisited over the past few years, with a tremendous number of innovations that has enabled high voltage cathode chemistries.

Use of lithium metal anode in aprotic electrolytes, however, as depicted in Fig.1, has the problem of unstable electrodeposition during charging which has plagued this field over the past few years. Several approaches have been proposed for resolving this issue, including engineering the solid-electrolyte interface, careful design of electrolyte to formulate high modulus electrolytes that can suppress the dendritic growth and single ion conducting electrolytes that can stabilize electrodeposition. Solid electrolyte interface engineering has achieved significant attraction over the past five years, owing to its simplicity and ability to retain most of the original components of the cell design. The long-term goal however is to enable intrinsically stable solid-state electrolytes that can eliminate dendritic growth indefinitely. Polymer electrolytes have been considered for decades as the most attractive option for this purpose, due to their versality with respect to the different chemistries possible and the large room for engineering these systems. This is further explored in detail in chapters 2-4.

Design of solid state electrolytes

Although most of the lithium ion battery development was initially focused on the electrode development as they determine the energy densities, it was quickly realized that the electrolyte plays as important a role in realizing the said cell chemistries, as it is the electrolyte that determines the operating electrochemical window of the functioning cell. It also affects the power capability due to its resistance, both in the bulk and at the interfaces formed with the electrode and separator. It is for this reason remarkable that while significant innovations in chemistry have been deployed to evolve the storage characteristics and capacity of the cathodes used in LIBs over the last 30 years, there hasn’t been much deviation from the classical formula of using carbonate based aprotic solvents with Lithium salt as the electrolyte.

With increasing energy densities made possible by innovative cathode chemistries that enable cell operation at higher potentials and the use of lithium metal as the anode, these conventional electrolyte designs are under significant threat both as a result of their poor reductive stability in extended contact with a metallic Li anode and their limited oxidative stability in contact with a high voltage cathode. With broader deployment in transportation, the possibility of explosions and fire hazards posed by carbonate-based electrolytes have also become an important galvanizing force for change.

Solid state electrolytes have long been considered the ultimate solution to the most difficult of these problems, because reaction kinetics of the chemical and electrochemical reactions that cause a liquid electrolyte to fail are substantially slower in a solid electrolyte. Fig 1.3[3] summarizes the different types of solid state electrolytes explored so far. Apart from their effectiveness in suppressing dendritic growth as discussed in the previous section, they have high operating electrochemical stability windows and high temperature stabilities.

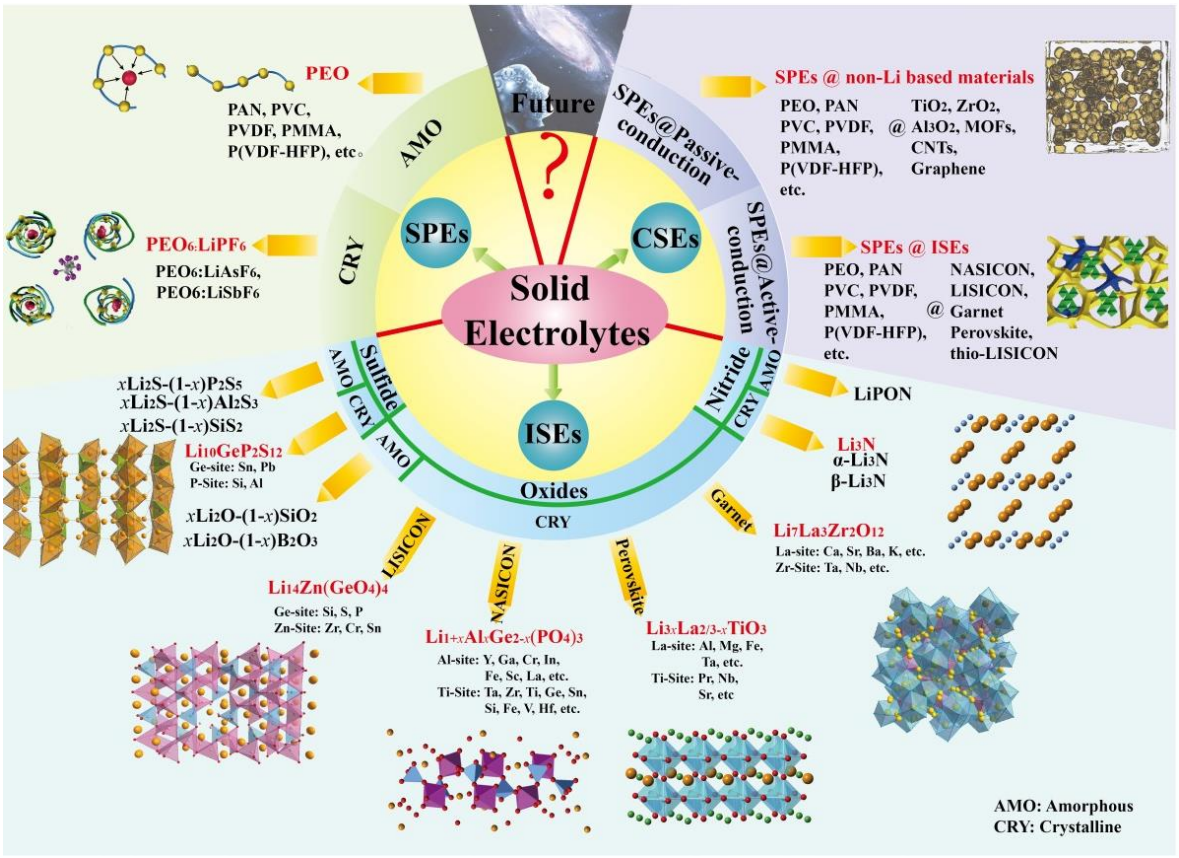

Fig 1.3 Different solid-state electrolyte configurations[3]

The materials in the figure are seen to fall in two broad categories: solid-state inorganic and solid-state organic electrolytes. Inorganic solid-state electrolytes include ceramics and glasses, which possess vacancy and interstitial defects and these atomic structure disorders enable conduction of alkali metal ions. These materials offer high thermal and mechanical stability and are often single-ion conductors, possessing near unity Li^+ transference numbers. Examples include NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $0 < x < 3$), LIPON ($Li_xPO_yN_z$, $x=2y+3z-5$), LLZTO ($Li_7La_3Zr_{2-x}O_{12}$) and β-alumina. A drawback of many inorganic solid-state electrolytes is their low room temperature conductivities, which have largely limited their application to thin-film batteries, where the impact of electrolyte resistance on power density delivered by the battery is substantially reduced owing to small thicknesses. Inorganic solid-state electrolytes also have

poor electrode/electrolyte interfacial contact due to their low plasticity, making their commercial scale applications cumbersome. Cost, sensitivity to moisture and oxygen during battery assembly, and tendancy to crack during battery assembly pose additional challenges to their large-scale implementation in batteries.

Organic solid-state electrolytes, dominated by polymer-based materials, take advantage of inherent thermoplastic features and processability of polymers to overcome many of these limitations. This class of electrolytes nonetheless introduces other challenges associated with poor room temperature ion transport characteristics and chemical instability of the interfaces formed between the electrolyte and electrodes in a battery. This thesis is motivated by the need for fundamental understanding of these challenges and by opportunities offered by cross-linked polymer systems, which may/may not host a liquid present for overcoming them.

Structure of this thesis

This thesis begins with a brief introduction about current state of lithium-based battery technologies (Chapter 1). It then discusses the three different kinds of polymer electrolytes and the ion conduction mechanism in these systems, with a small discussion about the techniques used to characterize them (Chapter 2). We then proceed to investigate the synthesis, characterization, and performance of one of the three types of polymer electrolytes, namely crosslinked polymer electrolytes (Chapter 3). Finally, Chapter 4 presents a study of a class of crosslinked multifunctional polymer gel electrolytes derived from ideas discussed in Chapter 1-3.

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CHAPTER 2: POLYMER ELECTROLYTES

Polymer based electrolytes can be classified into three types: Dry Polymer electrolytes, Gel polymer electrolytes and Composite electrolytes. A brief overview of the three different kinds of polymer electrolytes are presented here, following which the ion conduction mechanism in each is explained. The characterization tools used in the study are later briefly elaborated.

Dry Polymer Electrolytes

Dry polymer electrolytes are systems in which a polymer, traditionally polyethylene oxide (PEO), and a lithium salt constitute the entire electrolyte. Polyethers are attractive because they dissolve metal salts by complexation of the metal cations, via non-covalent interactions between lone pairs on the ether oxygen and the lithium ion. Many factors affect this interaction such as the nature of the functional groups on the polymer backbone, their distribution, the polymer molecular weight, degree of branching, and the solvating power of the counter ion of the salt. Although ionic conductivities achieved in such materials are normally too low to support room-temperature battery operation, their ion-conduction mechanisms have been widely investigated to develop strategies for improving it. PEO polymers are semi-crystalline in nature, containing both crystalline and amorphous regions. While most reports suggest that ion conduction is facilitated by segmental motion of repeat units along the polymer backbone in the amorphous phase [1,2], a small number of studies show that lithium ion conduction can also occur through lattice defects in the crystalline phase of

polymers[3–5]. Bruce and co-workers, for example, reported that the crystalline phase of PEO is composed of tunnels formed from pairs of $(CH_2–CH_2–O)_n$ chains, within which the Li^+ ions reside and along which they may migrate. In this picture, the anions are thought to maintain electroneutrality by residing outside the tunnels. The authors argued that the ionic conductivity in these ordered environments is dominated by the mobility of cations, which leads to higher cationic transference numbers. However, this ionic conductivity is almost two orders of magnitude lower than that observed in the amorphous phase, which explains the dominant role molecular diffusion of polymers has played in our understanding of ion transport in polymer electrolytes. It also explains why the most successful approaches for improving polymer conductivity have relied on strategies to suppress crystallinity. The ion conduction mechanism of Li^+ cations in polymer electrolytes is shown in Fig 2.1.

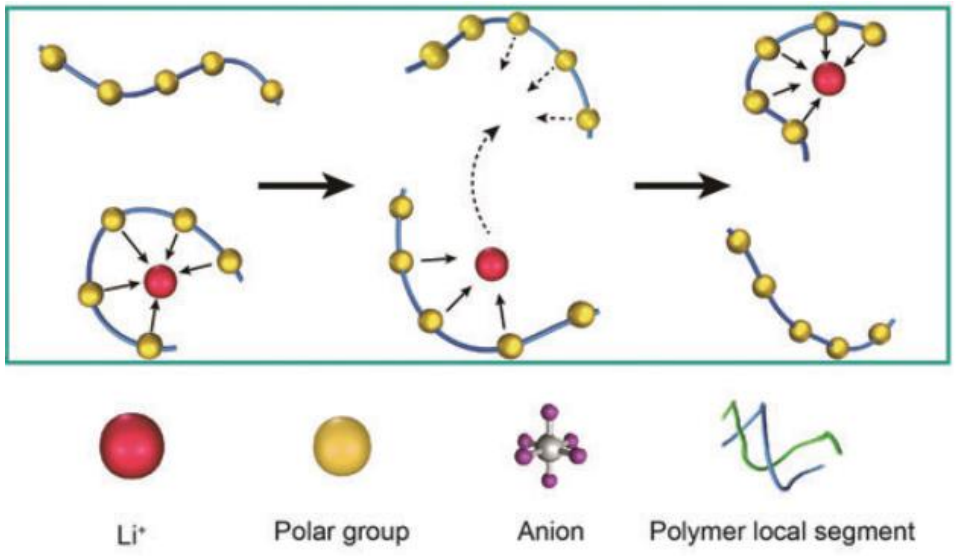

Fig 2.1 Ion conduction mechanism of Lithium salts in polymers via segmental motion of polymer chains and ion cluster motions

It can be seen that motion of lithium ions in the materials occurs in tandem with segmental motions along the polymer chain backbone. The polar ether oxygen groups are thought to coordinate with the lithium ions, facilitating their dissociation, but at the same time couples long-range motion of the ions to dynamics of polymer chain segments and to the overall ease with which ions hop from one coordination site to another. The motion of ions in polymers would then be expected to manifest two energy barriers. First, the hopping from one coordination site to another, which is dependent on the motion and microscopic viscosity of the polymer chains, can be described using the Vogel Tamman Fulcher (VTF) model, $\sigma = \sigma_o \exp[\frac{-B}{R(T-T_o)}]$. The VTF equation describes diffusion in disordered and glassy materials and typically represents a process where the ion hopping motion of the ions is coupled with the relaxation of the polymeric chains. Here σ_o is the prefactor describing the charge carrier concenration, B is an apparent activation energy and T_o is a reference temperature, which is typically 50K below the polymer glass transition temperature. Li+ ions can also move in the polymer host as a result of breaking and formation of coordination bonds. Transport by this mechanism is decoupled from segmental scale dynamics and follows Arrhenius behavior, $\sigma = \sigma_o \exp\left[\frac{-E_a}{RT}\right]$, where E_a is the activation energy. The Arrhenius behavior is observed in systems where the ion hopping is decoupled from the segmental motion of the polymer, for example in the crystalline phase of the polymer and in inorganic solid-state electrolytes. In typical temperature ranges where polymer electrolytes operate in batteries, the first of the two mechanisms

is consistently the more dominant and polymer segmental motion heavily influences the conductivity of the electrolyte, implying that VTF behavior is dominant.

The inherently slow dynamics of polymer chains and strong coordination to Li+ ions are therefore the source of generally poor room temperature ionic conductivity values reported for polymer electrolytes. Strategies to overcoming this fundamental limitation of polymers has been a major area of research since the conception of polymer electrolytes by Wright and co workers in 1973. Although the high modulus, dual function as separator and electrolyte and processability of dry polymer electrolytes makes them the holy grail of next generation solid state battery technologies, poor conductivity and interfacial adhesion of these systems have impeded their large-scale applications and commercialization to a great extent. Gel polymer electrolytes and composite electrolytes have provided attractive improvements over dry polymer electrolytes over the past few years, capable of overcoming these shortcomings.

Composite polymer electrolytes

Polymer composite electrolytes composed of a filler and a matrix/solvent have obtained great attention over the past few years due to their versatility and room for tuning. While the ceramic fillers can improve conductivity by various means, they also impart additional mechanical strength due to their inorganic core. Each component retains its own properties which can be tuned due to a large number of degrees of freedom, while new characteristics arise due to interactions between the various

components. The fillers have also shown to improve interfacial adhesion and better surface conductivity as compared to gel/solid polymer electrolytes.

Croce *et.al*[6] first reported inorganic-organic hybrid polymer electrolytes, where nanometer sized ceramic Al_2O_3 and TiO_2 particles were added to PEO-$LiClO_4$ mixtures as a solid plasticizer. This was a game changer, where conductivities of the range 10^{-4} were obtained at 60°C (Fig 2.3), never before observed in an electrolyte without liquid plasticizers.

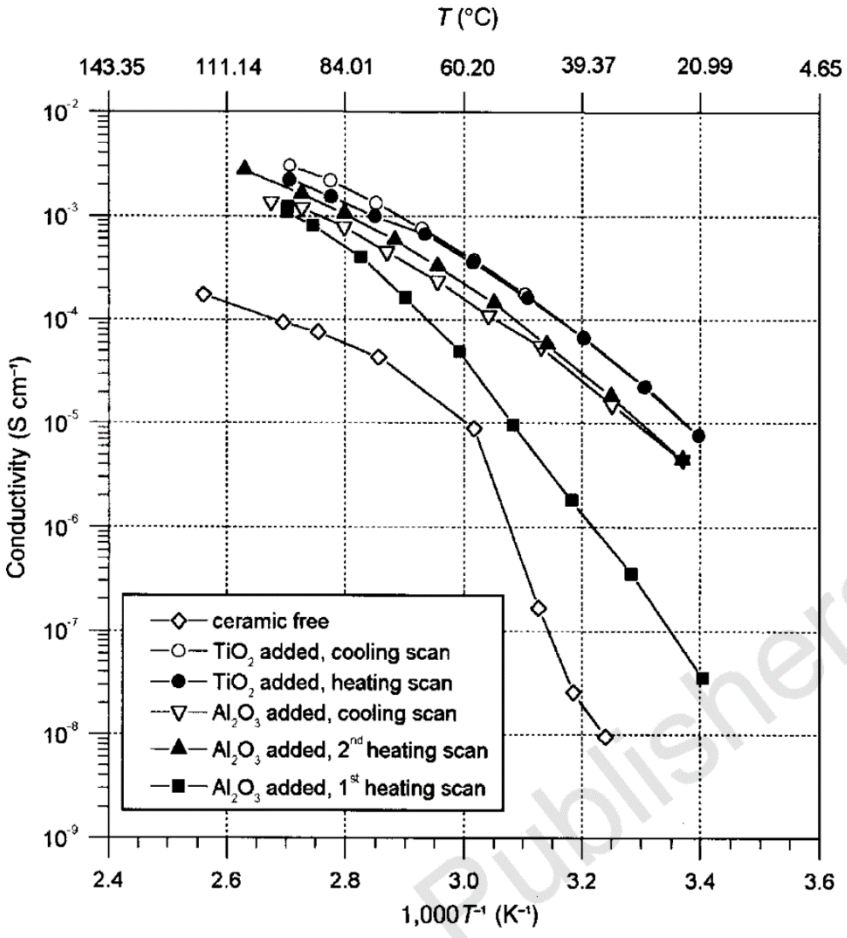

Fig 2.3. Conductivity vs temperature for PEO-$LiCLO_4$ electrolytes with different ceramic fillers[8]

Various mechanisms for the ion transport improvement in these systems have been proposed. Croce *et.al* finally concluded that there are two possible ways by which the fillers improve ion transport in these sytems: They can act as crosslinking centers for the PEO segments and the anions, thereby reducing crystallinity and promoting Li^+ ion transport, and they also increase ion pair dissociations by acting as sites of Lewis-acid base interactions for the ions.

Since then, different architectures of polymer nanocomposites have been reported in literature. Liu *et.al* reported solid composite polymer electrolytes with well aligned nanowires which exhibited exceedingly high ionic conductivities[7]. They argued that this was due to fast ion transport along the highly conductive nanowire surfaces. Zhang *et.al* reported nanostructured electrolytes in which liquid electrolytes were confined within hollow nanospheres to yield solid electrolytes with extremely high modulus and liquid like conductivity. The hollow sphere nanoarchitecture allowed ample room for tuning the flexibility and chemistry of the system for application in different battery technologies.

One of the main advantages with ceramic fillers is the ability to modify the surface chemistry to accommodate different functionalities. This particular aspect was cleverly exploited by Schaefer *et al,* whereby single ion conducting electolytes were created by co-tethering sulfonate groups along with PEO oligomers on silica nanoparticles.[8](Fig 2.4). When dispered in a tetraethylene glycol matrix with lithium salt, the transference numbers obtained were close to 1, due to the immobility of the bulky anions in the elctrolyte.

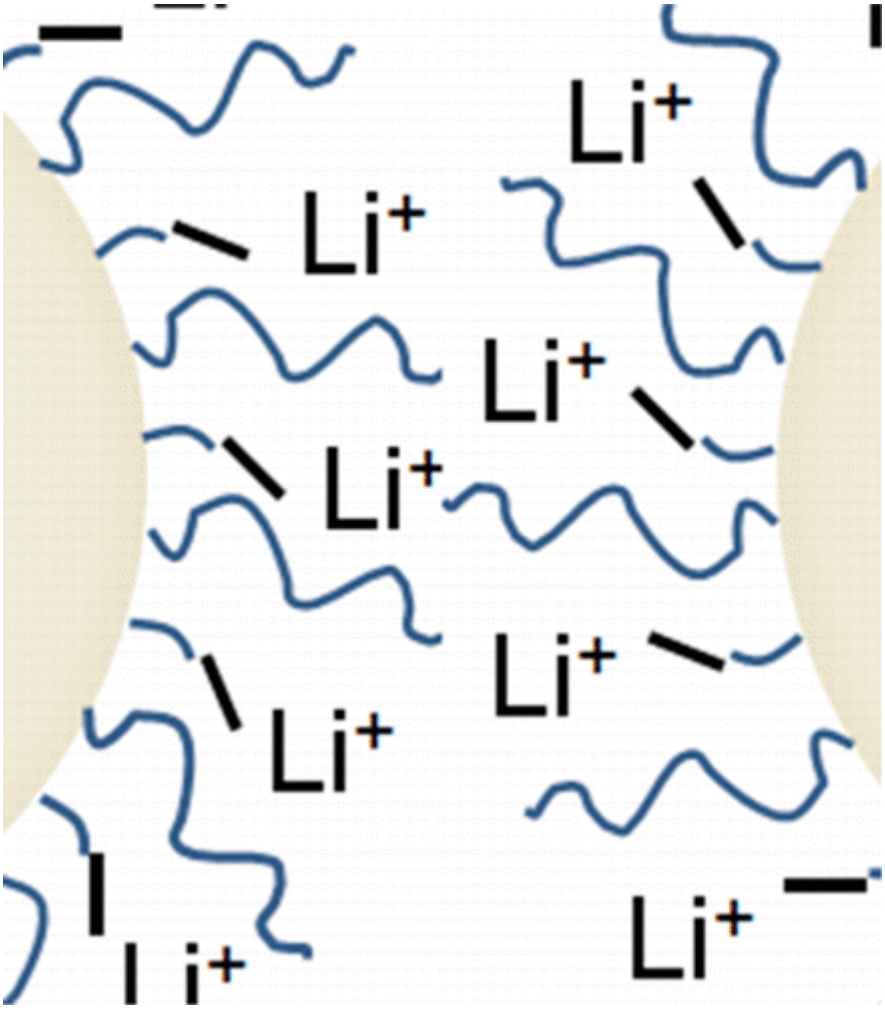

Fig.2.4 Single ion conducting electrolyte created by grafting sulfonate and PEO chains on silica nanoparticles[10]

The idea of tuning the surface chemistry to enable “active fillers” has been widely investigated ever since and recently, Zhao *et.al* PEO electrolytes with high transference number by using garnet type LLZTO particles. Such particles, when dispersed in a high molecular weight PEO, are thought to simultaneously suppress

crystallinity and to immobilized the $TFSI^-$ anions due to their strong interaction with TFSI[9].

Despite numerous reports detailing the effects of fillers in improving conductivity and retaining mechanical stability, achieving practical conductivity values at high loading of the fillers, where the mechanical modulus is maximized, has proven cumbersome and two decades of focused research on this issue has been unsuccessful. Hybrid hairy nanoparticles based on polymer tethered nanoparticles have shown significant promise towards solving this issue. Acting as active fillers, they exhibit attractive properties like thermal jamming, viscoelasticity and star polymer like relaxation.

Agarwal *et.al* reported such an electrolyte, where the polymer was confined at one end to the nanoparticle core, and dispersed in a Propylene Carbonate(PC) solvent media[10]. They found that the composite electrolyte showed a maximum in terms of conductivity vs volume fraction and showed jamming behavior under oscillatory shear measurements. Jamming is a convenient and attractive feature for an electrolyte, since they can be processed at a strain above the yield strain, while still remaining solid under static conditions in a batttery. Choudhury *et.al* also found that these hybrid hairy nanoparticle based electrolytes are effective in stabilizing electrodeposition in lithium metal batteries[11]. They argued that due to the spontaneous adsorption of particles on the surface of lithium metal, it forms a tortuous porous coating on the anode which prevents side reactions with the bulk electrolyte and limits electrodeposition to length scales comparable to the average pore size of the nanoporous electrolyte.

Due to the scale and room for nanoengineering of properties of composite/hybrid polymer electrolytes, they are considered as the future of solid state batteries. Significant improvement on optimization and synthesis of such electrolytes for high voltage cathode chemistries however still remains to realize large scale commercialization. Attempts at improving upon these aspects in polymers by blending with them with solvents to create gels have proven to be more successful.

Gel polymer electrolytes

Gel polymer electrolytes comprise of polymer-salt mixtures plasticized by a certain amount of liquid or organic solvent. The polymers form a gel network either by physical and/or chemical cross-links between individual chains. At sufficiently high polymer molecular weights, for example, a combination of topological constraints (*entanglements*) and ionic interactions between polymer chains mediated by salt causes the polymer to form a cross-linked network. Alternatively, the polymer chains can be crosslinked covalently to form the network. Plasticization by the liquid component decreases crystallinity and provides an additional mode (free-solvent) for fast transportation of ions in the electrolytes. The cross-linked materials possess cohesive properties analogous to those in the solid polymer, but at the same time have diffusive properties similar to those of liquids. This balance of properties imparts attractive tunability by varying the structure and chemistry of the liquid and solid components.

As alluded to in the previous section, gel polymer membranes can be broadly classified into two types. First those composed of a liquid solvent trapped in the porous structure formed by covalent, topological, or ionic cross-linking polymer chains, whereby the liquid component's characteristics mainly dominate the ionic conductivity. Second those in which polymer membrane is a homogenous system, whereby the swollen gel phase dominates ion conduction[12]. It is unsurprising that that the most common types of gel polymer electrolytes employed in lithium batteries are the simplest — physical mixtures of high-molar-mass (entangled) polymer chains with plasticizers with high dielectric constants (e.g. Ethylene Carbonate and Propylene Carbonate). [13,14] An inherent attraction of this material design is that the liquid component in the electrolyte can to a large extent be chosen independent of the polymer architecture. And, because the liquid makes the most intimate contact with the battery electrodes, the redox stability of the gel polymer electrolyte are often close to the values for the liquid component. Additionally, the gels are in the form of soft solids, with much higher conductivities than their host polymers, which makes them better interphase formers than either inorganic solid-state or neat solid-state polymer electrolytes. A perhaps obvious drawback, however, is that incorporation of volatile organic solvents in the materials to maximize bulk ionic conductivity come at the price of compromised safety.

Electrolytes created by blending polymers and ionic liquids have emerged as an important class of fluids as alternatives to those in which polymers and organic solvents are combined. The ionic liquids, apart from improving the conductivity of the

electrolyte, are also reported to improve the voltage and thermal stability of the system. Few studies have also reported that imidazolium based ionic liquids interact favorably with PEO, via hydrogen bonding with the ether oxygen moieties[15]. This provides an added benefit, since the imidazolium cation can compete with the lithium ion for coordination, thus reducing the energetic requirement for breaking and reforming coordination sites with the polymer backbone; enhancing ion conduction by the cation hopping mechanism. Indeed MD simulations have shown that such blends display higher Li^+ cation diffusivity values, compared to pristine PEO/Li salt mixtures[16]. Ionic liquids also provide other benefits, including their ability to serve as supporting electrolytes, whereby they can reduce ion polarization in a battery, maintaining high ionic conductivities even at high current densities. This feature is not well studied in the literature, but provides an important platform for improving cycling efficiency of batteries and for minimizing dendrite formation in LMBs at current densities above the diffusion limits. An ongoing challenge with these and all polymer-based electrolytes concerns the need for improving mechanical integrity of the materials to avoid the use of a separator (which adds to cell mass and cost) and to avoid leakage of the liquid component, which limits the range of form factors in which batteries using such electrolytes can exist.

Electrolytes in which polymer chains are covalently cross-linked have emerged as potential solutions, in which desireable features of polymers are maintained. Cross-linking of polymers by methods such as, UV, thermal radiation and photo-polymerization reduces the solubility of the polymers with the organic solvents and

traps the liquid within the pores of the polymer network. Tuning the monomer size, polymer chemistry and reaction conditions can result in a whole library of network structures with different pore sizes, modulus, and wettability. By trapping the liquid solvent within the pores, problems of leakage and reduction in modulus is avoided[17]. For example, this is illustrated in Fig 2.2, where hydroxy terminated PEO functionalized hairy nanoparticles serve as node points for crosslinking a PPO polymer. The membrane was then soaked in a commercial PC electrolyte and proved highly efficient for room temperature operation of a lithium metal battery and the negligible compromise on mechanical integrity due to crosslinking proved useful in suppressing dendritic growth of the lithium metal[17].

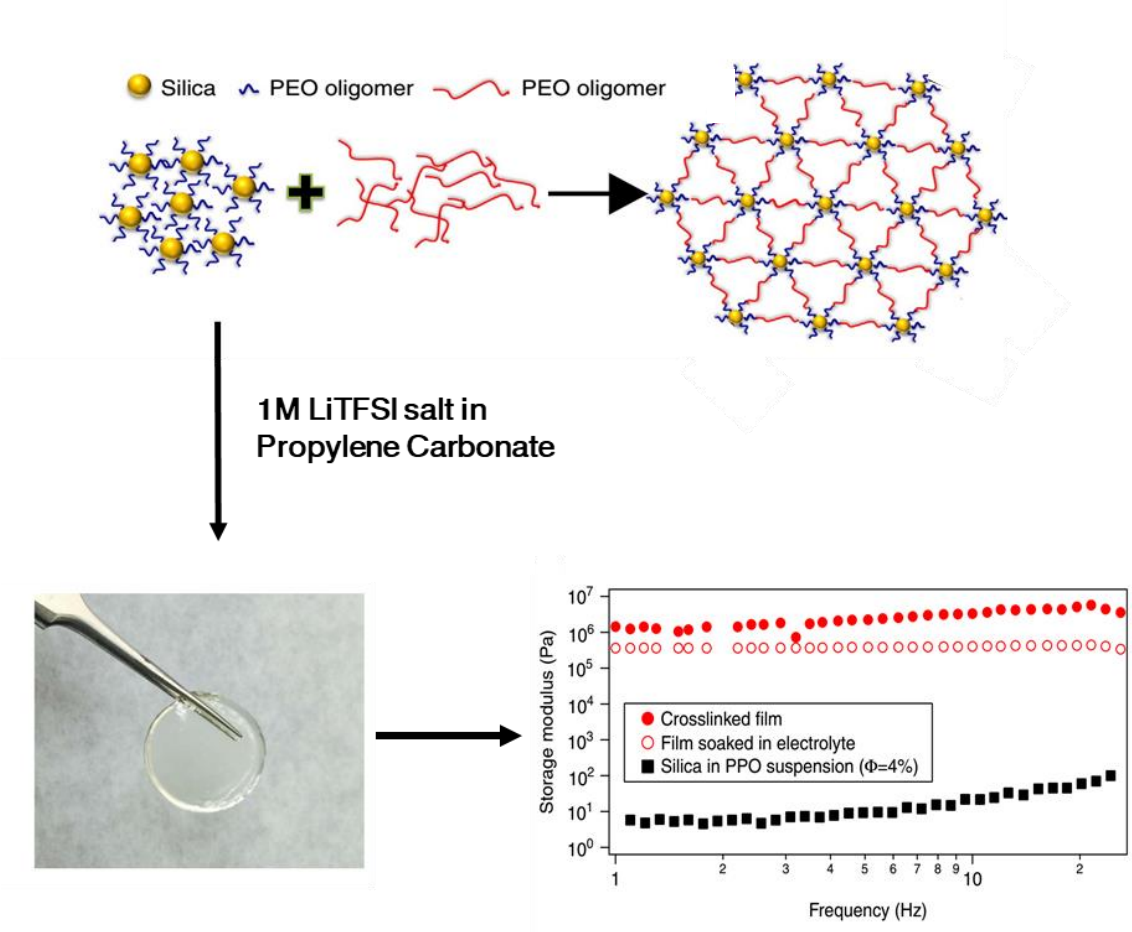

Fig. 2.2 Scheme illustrating preparation of hybrid crosslinked polymeric membrane. Upon soaking in commercial electrolyte, the reduction in mechanical modulus was observed to be only a mere factor of 3[10]

Crosslinking of polymers is also a way of reducing the volume of crystalline phase, while at the same time increasing storage modulus of the system. By introducing monofunctional monomers along with difunctional monomers prior to crosslinking, pendant chains can be introduced into the network, whereby different functionalities can be incorporated into the network for imparting properties like ion rectification and flame retardancy. This is further elaborated in Chapter 3 and 4.

Characterization Techniques

Differential Scanning Calorimetry

The relation between conductivity and polymer segmental dynamics are studied throughout the thesis using Differential Scanning Calorimetry(DSC). In DSC, the amount of heat required to raise the temperature of a sample with respect to a reference is measured as a function of temperature. When the sample undergoes a phase transition, such as melting or crytallization, more or less heat flows to maintain the same temperature as the reference. Measurement of the heat flow therefore provides useful information about the phase transitions. During melting, which is typically an endothermic process in polymers, the heat flow is positive compared to the reference. In a exothermic process like crystallization, the heat flow is negative. DSC also allows one to characterize more subtle transitions associated with temperature-dependent changes specific heat capacity and dielectric constant associated with changes in molecular packing and dynamics such as those that accompany the glass transition in polymers. At the glass transition, short-range segmental motions become highly restricted and long-range polymer diffusion is completely arrested. This causes a physical transformation of a polymer electrolyte from a flexible rubbery texture to a macroscopic glass. During such a second order transition, the properties of the polymer like specific heat, dielectric constant and free volume changes. There is no heat transfer to the surrounding, but rather slow change in free volume of the sample. In this case, the observed change in heat flow is in the form of a shift in baseline, as shown in Fig 2.5.

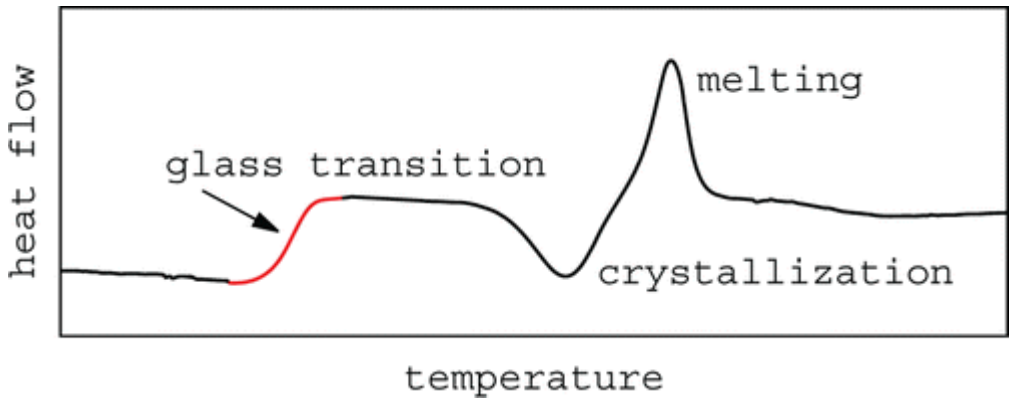

Fig.2.5 Different phase transitions observed in DSC measurements for polymers[18]

Dielectric Spectrometry

Dielectric spectroscopy is used in the study to measure the dielectric and electric properties of electrolyte media as a function of frequency. When an external electric field is applied, the dipoles in a material respond by orienting in the field. In materials containing mobile ions, the field can also cause redistribution of charges, which manifest as time-dependent changes in dielectric properties of the studied materials .

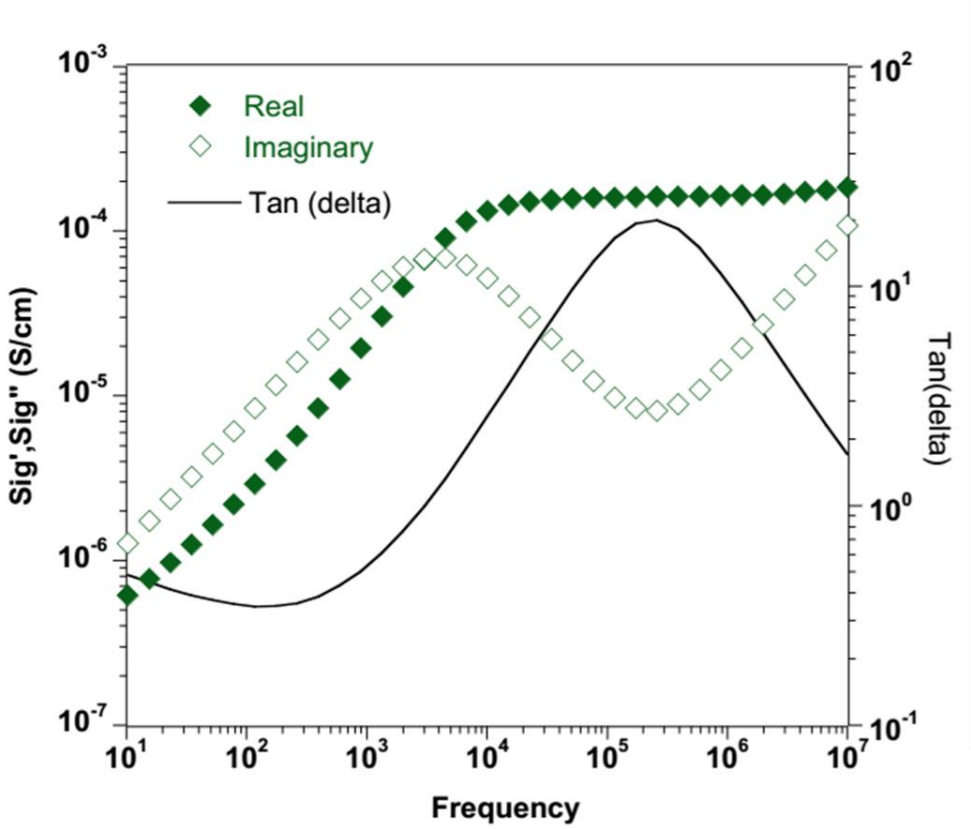

Fig 2.6 Dielectric response of a crosslinked polymer electrolyte[19]

Fig 2.6 shows typical Dielectric response of a crosslinked polymer electrolyte[19]. The ionic relaxation of ions in an electrolyte are due to interfacial and space charge relaxations. The plateau at high frequencies, comprising of relaxations at short time scales, correspond to bulk conductivity and long range ionic motions while the plateau at low frequencies, representing relaxations of long time scales, correspond to the space charge layer relaxation at the interface of the electrode and electrolyte. However, the conductivity response one obtains from dielectric spectroscopy is due to the net ionic conductivity, due to the movement of cations and anions. The ionic

conductivity is related to self diffusion cofficient of the individual ions through the Nernst-Einstein equation,

$$\sigma = \frac{F^2 C}{RT} (D_+ + D_-) = \sigma_+ + \sigma_-$$

By coupling results from dielectric spectroscopy and techniques like NMR spectroscopy to determine diffusion coefficients, we can obtain the individual cationic and anionic conductivity values.

Dynamic Mechanical Ananlysis

Dynamical Mechanical analysis is used to study the viscoelastic behaviour of polymeric materials. The complex modulus of the material is obtained by measuring the strain following the application of a sinosoidal tensile stress. The stress strain relationship gives us information about the viscous and elastic components of the material. In case of purely elastic materials, the strain and stress are in phase while in case of a purely viscous material, the strain and stress are out of phase.

Properties of polymers like chemistry, degree of crosslinking, pore size and molecular weight affect the tensile storage and loss modulus of the material.

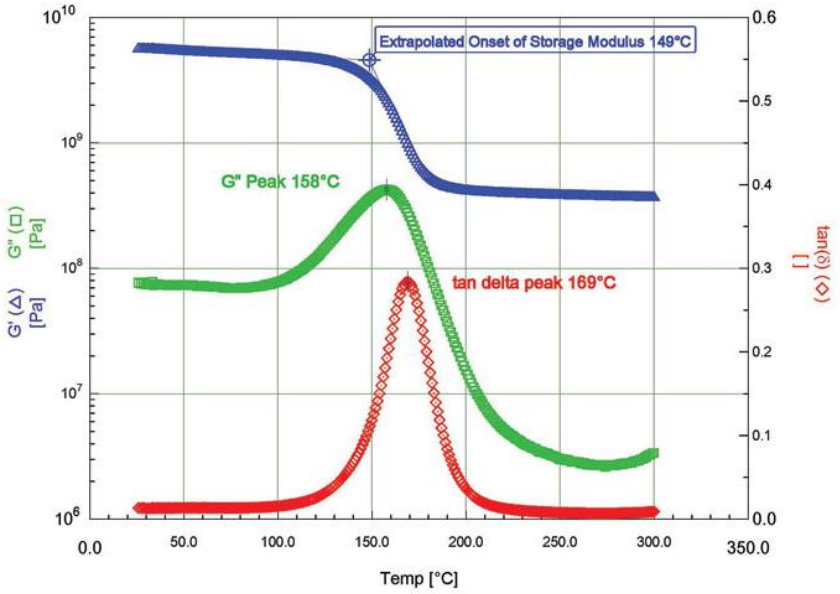

Fig.2.7 DMA measurment results for a viscoelastic material

Fig 2.7 shows typical DMA graph of storage and Loss modulus vs temperature for a viscoelastic material with a larger storage modulus than loss modulus[20]. The decrease in internal stresses and increase in free volume at higher temperatures leads to the glass transition, whereby we can obtain the rubbery plateau modulus of the polymer.

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CHAPTER 3

Enhancing ion transport in polymeric networks via pendant chains

Introduction

Crosslinked polymers have been increasingly studied as membranes for applications in drug delivery[1], fuel cells[2], separation processes[3] and recently energy storage[4]. Crosslinking of polymers leads to enhancement of physical and chemical properties, including increased thermal, mechanical and chemical stability against degradation like oxidative decomposition. Electrolyte membranes composed of Polyethylene oxide have long been considered the most attractive alternative to traditional volatile and combustible liquid electrolytes due to their ability to coordinate with alkali metal ions, their flexible nature and vast room for engineering different chemistries in the electrolyte. However, their room temperature conductivity is heavily compromised due to the crystallinity of the host polymer. One of the most effective ways of tackling this issue is the crosslinking of the backbone, which reduces the crystallinity and increases the amorphous phase in the polymer, leading to a rubbery material. This also introduces a lot of degrees of freedom in the network, which can be utilized to crosslink monomers of different chemistries and physical properties to create a whole library of different materials with tunable properties.

One common class of crosslinking chemistry often looked at for this purpose is the acrylate-acrylate polymerization chemistry. Polyacrylates are dimensionally stable

and are also heavily used for reinforcement in polymer gels. Long range transport is enabled by the ether oxygen groups on the backbone while structural properties are enhanced by the vinyl ester network[5]. The high reactivity of the acrylate group also enables fast polymerization upon initiation by a heat source or UV light leading to creation of mechanically robust and homogenous networks. By introducing monofunctional monomers within the precursor before crosslinking, one can easily alter the properties of the base network.

Herein, we report the effect of such grafted pendant chains on physical and subsequent ion transport properties within a crosslinked acrylate-based network. It is noticed that the higher mobility of the pendant chains and the improved free volume in the network facilitates transport of ions in the bulk and at the electrode/electrolyte interface.

Results and Discussions

The synthesis scheme adopted for the polyethylene glycol-based networks is described in Fig 3.1. Typically, Polyethylene glycol dimethacrylate (PEGDMA) (Molecular weight=550) was mixed with different fractions of Polyethylene glycol monomethyl methacrylate (Molecular weight=360) which served as the pendant chains in the network .

Effect of pendant chains on physical properties of polymeric network

To study the effect of the pendant chains on the physical properties and phase transitions of the network, DSC analysis was performed at a scan rate of 10^{o}C. The DSC thermogram for the pure PEGDMA network is shown in Fig 3.2. One can see the

absence of any melting or crystallization peaks, and this has been classically attributed to the disruption in crystallinity of the host polymer due crosslinking. The glass transition temperatures of the various networks with different molar ratios of pendant chains is reported in Fig 3.3. One can observe that there is a monotonic decrease in the glass transition temperature with increasing fraction of pendant chains. Pendant chains in the network have long known to increase the available free volume in the network, due to the increase in porosity, decrease in crosslink density and enhanced mobility of the dangling chains. The glass transition temperature directly dictates the ion transport properties in the polymeric network, due to the coupling of ion motion and segmental relaxation of the polymer chains. This is further discussed in the coming sections, whereby it is seen that the enhanced mobility of pendant chains facilitates ion transport both in the bulk and at the interface.

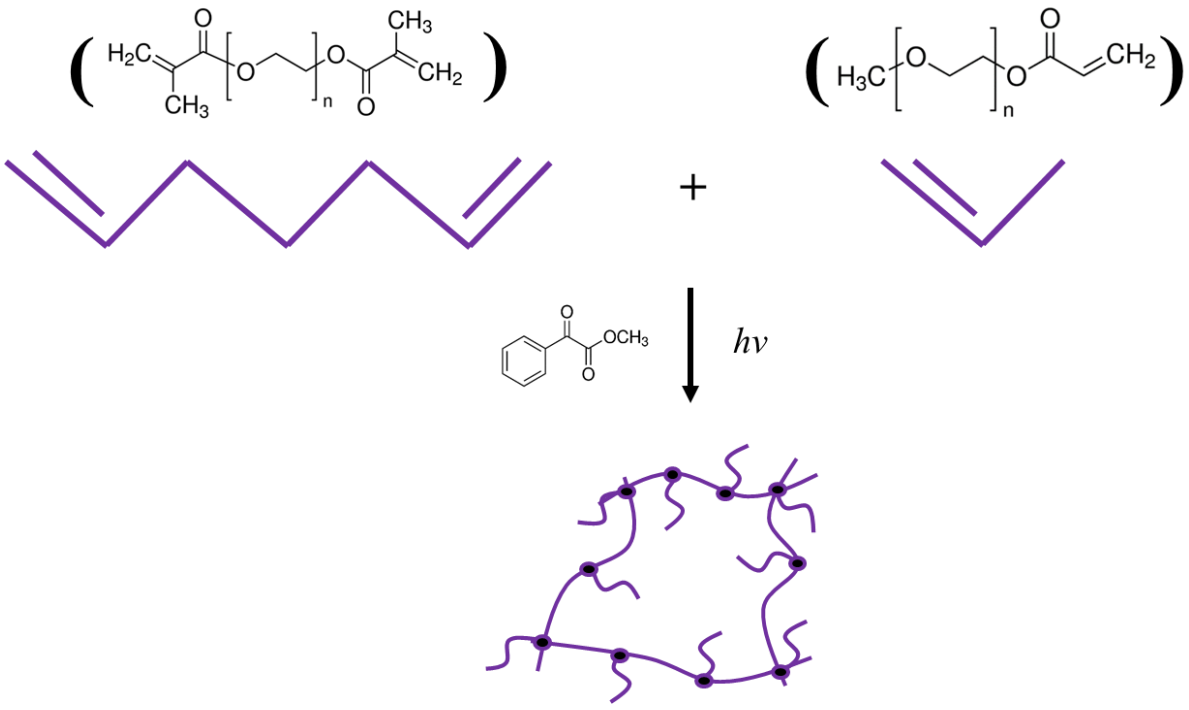

Fig 3.1 Schematic diagram for synthesis of crosslinked PEGDMA networks with pendant chains

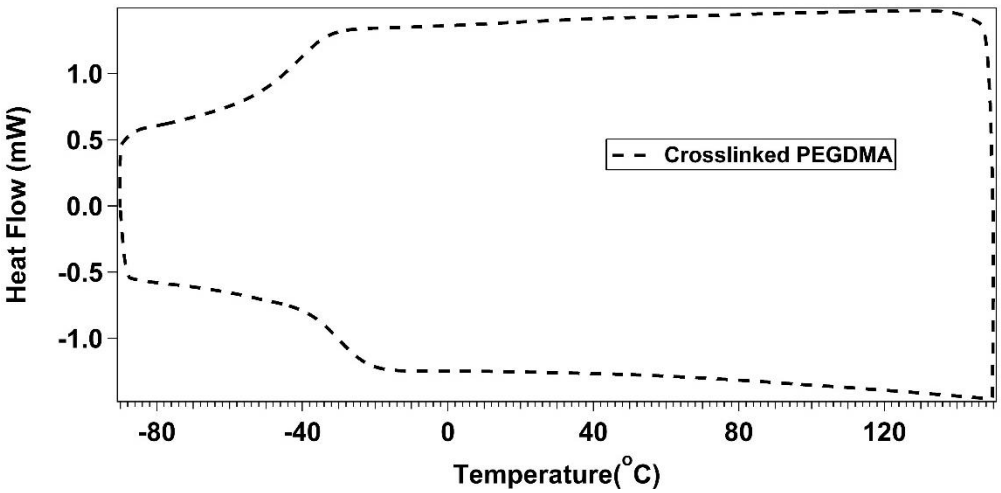

Fig 3.2. DSC thermogram for crosslinked PEGDMA network

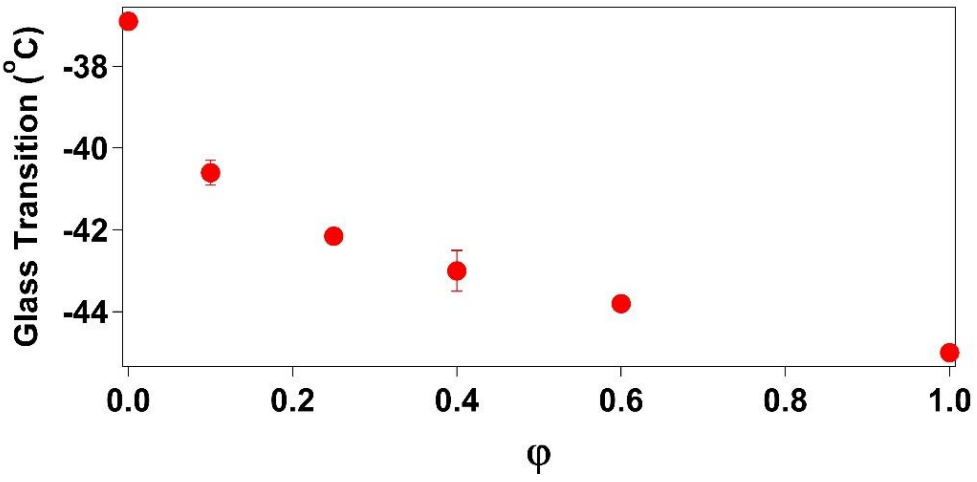

Fig 3.3. Glass Transition temperatures for networks with varying volume fractions of pendant chains

Effect of pendant chains on ion transport:

In order to study the ion transport properties in the bulk and at the interface of the electrolyte, the crosslinking precursor along with a predetermined amount of LiTFSI was directly drop-casted between two lithium electrodes and cured under a UV-Lamp in a glovebox for 20 minutes. This setup is illustrated in Fig.3.4, and was adopted to prevent contact issues typically associated with the electrode-electrolyte interface in solid state electrolytes.

To determine the optimum amount of salt to be added to the precursor, a set of control experiments were performed, whereby different amounts of lithium salt was added to the precursor without any monofunctional monomers. The parameter which was varied in this case was the molar ratio between the ether oxygen moieties on the polymer backbone and the Li^+ cations. Conductivity measurements were performed using dielectric spectroscopy following crosslinking of the precursors. The temperature dependent conductivity results are shown in Fig 3.3. A maxima behavior is observed, whereby the conductivity increases till a molar ratio of 18 (EO: Li), and then decreases. This maxima behavior is a well-known phenomenon and is commonly attributed to the fact that the salt concentration at lower molar ratios is insufficient to produce full complexation with all the available ether-oxygens, while at higher than the optimum ratio of 18, LiTFSI partially exist as undissociated and

non-conducting. For subsequent measurements with the incorporated pendant chains, this molar ratio between ether oxygen and lithium ions was kept constant.

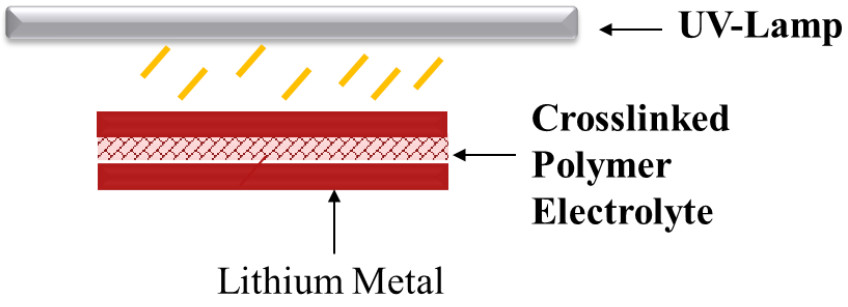

Fig 3.4 Setup used for UV-Crosslinking of precursor to form solid electrolytes

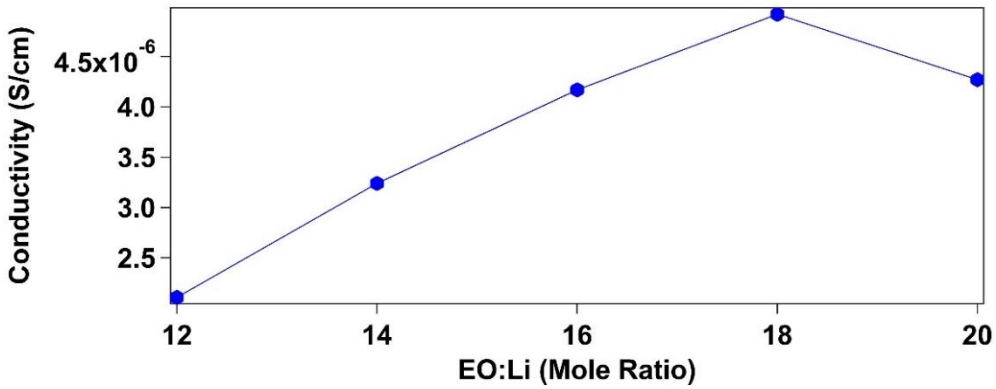

Fig 3.5 Room temperature DC ionic conductivities for different EO:Li molar ratios

The temperature dependent DC conductivity for the different molar ratio between the difunctional and monofunctional monomers in the network is shown in Fig. 3.6. It can be clearly seen that the with increasing pendant chain fraction, the ion mobility in the bulk increases. This is directly related to the increase in free volume observed from DSC measurements. The solid lines represent fitting with the VFT equation, where the reference temperature was taken to be 50K below the glass transition. A good fit between the VFT equation and the experimental data indicates that there is no thermal degradation or any phase transitions occurring in the range of temperature testing which could lead to a change in the mechanism of ion transport.

To test the effects of the pendant chains at the electrode/electrolyte interface, the systems were subjected to Electrochemical impedance spectroscopy measurements. EIS is a commonly used technique to study the interfacial characteristics in a electrochemical cell where we apply a sinusoidal voltage and with the current response at different frequencies, we can characterize the underlying chemical processes occurring in a cell. The response can be fitted with a simple circuit model shown in Fig. 3.7, to separate the contributions from the bulk and interfacial processes. The circuit model chosen consists of a resistor (bulk resistance) in series with a capacitor/resistance couple which represents the interfacial contribution. A Warburg element is also included which represents mass transfer processes at the interphase. The interfacial resistance values obtained by fitting the raw data to the described circuit model is represented in Fig 3.8.

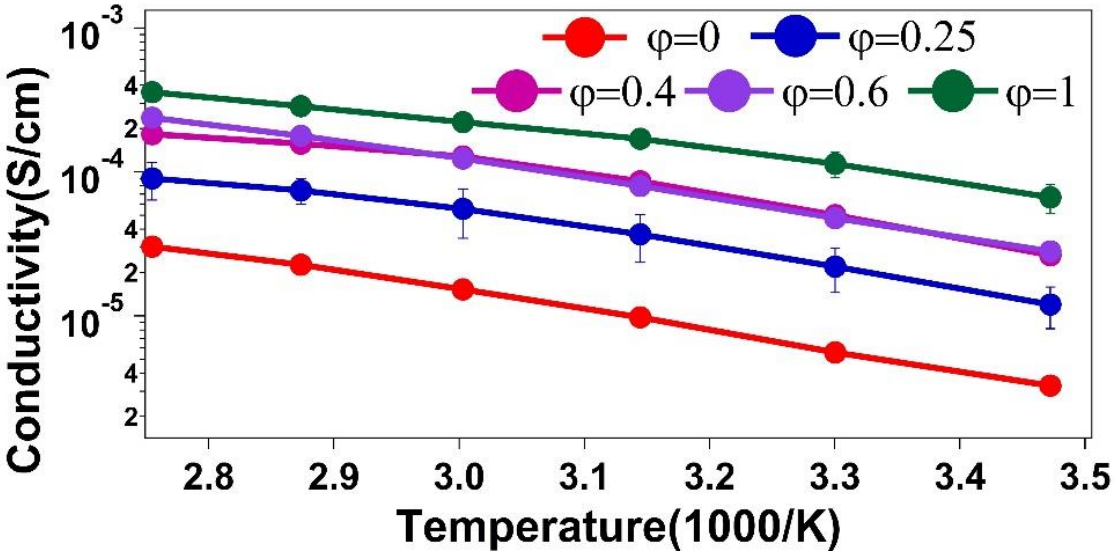

Fig 3.6: DC ionic conductivity as a function of temperature for different membrane electrolyte configurations

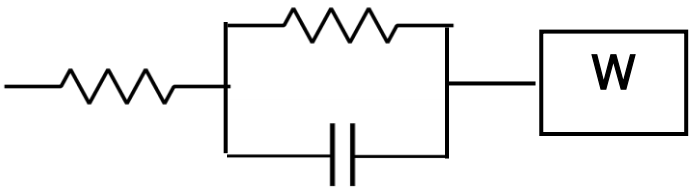

Fig 3.7: Circuit model for fitting raw impedance data to obtain interfacial resistance

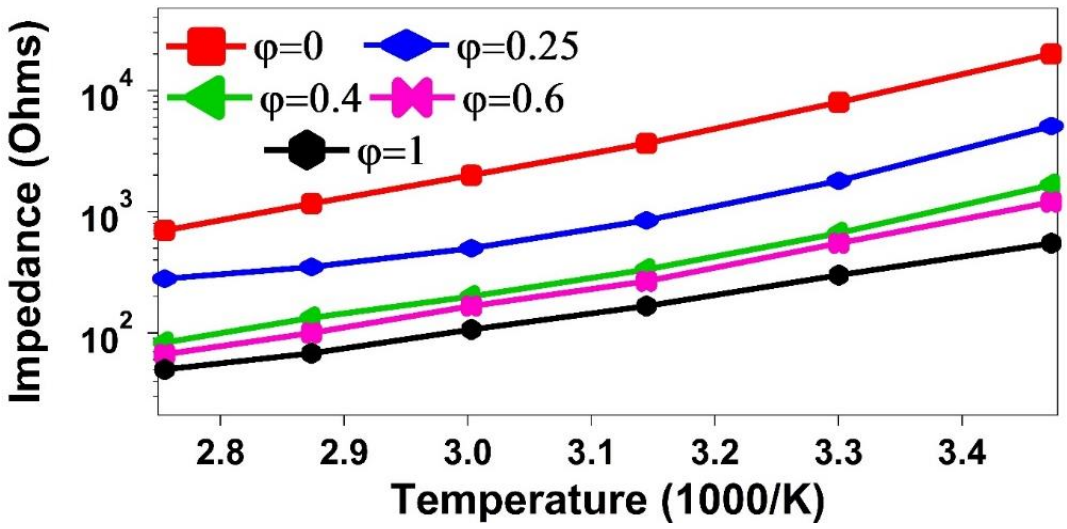

Fig 3.8. Obtained interfacial resistances from fitting as a function of temperature for different membrane electrolyte configurations

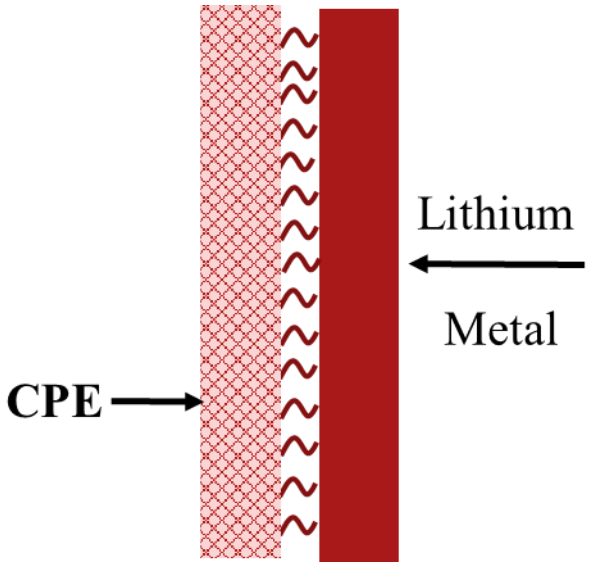

Fig 3.9. Illustration of possible interlayer at electrode/electrolyte interface formed by grafted pendant chains

Similar to the bulk, it was found that the pendant chains reduce the barrier for charge transfer at the interface. This can be understood by imagining the pendant chains to

form a interlayer at the electrode/electrolyte interphase, as depicted in Fig 3.9. It is possible that the free chains acting as an efficient interlayer provides a faster route for charge transfer between the two solid substrates due to their higher mobility. It is also worth mentioning that the interfacial resistance values were also found to fit with the VFT equation, indicating that there was no reactive degradation at the lithium metal electrode surface in the temperature range tested.

The VFT fits can also provide the activation energy for ion transport in the bulk and at the interphase. The obtained parameters for the different membrane configurations are shown in Fig 3.10.

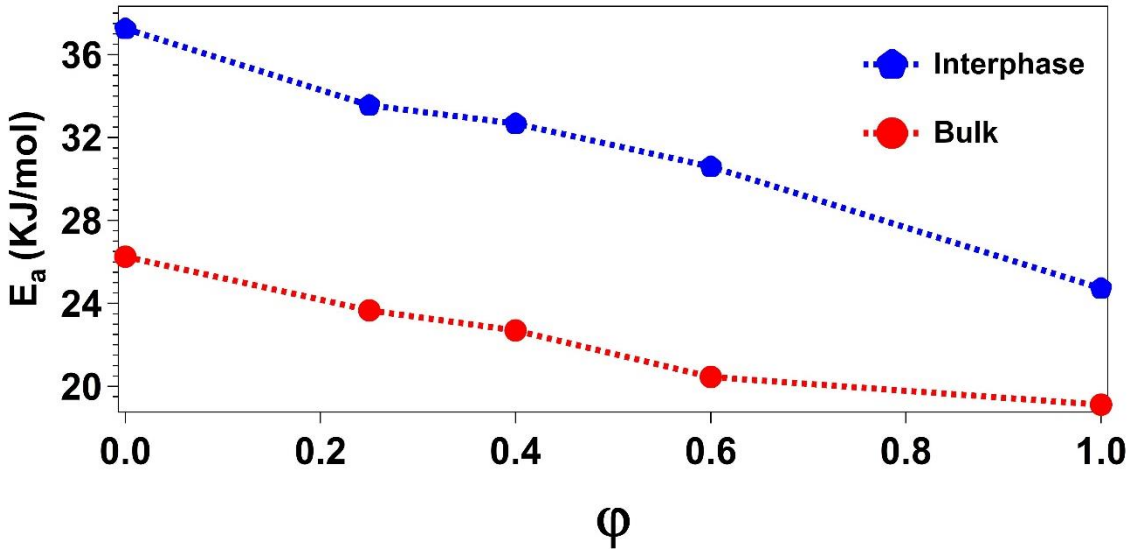

Fig 3.10. Activation energies for transport of ions in the bulk and at the interface obtained from fitting of data with VFT equation

The activation energy values are found to follow the same trend in the bulk and at the electrode/electrolyte interface, confirming that the same transport mechanism exists in

both regions and the energy barrier is reduced by the dangling chains. Strong coupling between the segmental motion of the dangling chains and ionic transport is thus evident. The values of the activation energies for charge transfer is higher than the bulk motion as expected due to reduced interfacial conductivity. However, it is worth noting the high activation energy values in these systems, compared to liquid electrolytes, which are typically of the order of 1KJ/mol. This emphasizes the importance of plasticizers and gelation of these systems, which can further increase the segmental motion of the polymer chains and increase solvation of the ions.

Conclusions

We have reported the formulation of crosslinked PEO networks based on acrylate polymerization chemistry as solid-state electrolytes. By varying the fraction of pendant chains in the network, enhancement of transport properties were observed both in the bulk and at the electrode/electrolyte interphase. This was mainly attributed to the high degrees of freedom of the dangling chains that reduce the barrier for ion hopping in the network. Using this framework, one can successfully incorporate multiple functionalities within said network, to influence the chemical properties aside from the physical properties of the electrolyte[6]. This is studied more in-depth in Chapter 4.

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CHAPTER 4

Multifunctional cross-linked polymeric membranes for safe, high-performance lithium batteries

Introduction

Since their introduction in the 1980s Lithium ion batteries (LIBs) have found wide spread applications in portable devices and are now poised to dominate electrified transportation technologies 1–4. Despite the relatively modest storage capacities intrinsic to the graphitic anodes and intercalating cathodes typically used in LIBs, researchers have over the last two decades made steady progress in increasing the energy density of LIBs largely through fundamental understanding of inorganic chemistry of the cathode, which has lead to steady increases in the operating potential of the cathode. It is remarkable that this progress has been made using the same volatile and combustible liquid electrolytes employed in the first-generation LIBs5–10. Accidents reported across the world in both hand-held devices and electric vehicle technology has brought new attention to the safety features of electrolytes in LIBs and underscored the need for fundamental materials chemistry approaches that address limitations of LIB electrolytes.

It is known that when a LIB is abused by electrochemical, mechanical, or thermal means, an irreversible thermal runaway reaction occurs that leads to catastrophic cell failure leading to a fire or explosion. This process is facilitated by degradation of the

oxygen-rich cathode chemistries that result in highest cell potentials and capacities, which may react directly with

solvent or disproportionate to produce oxygen which fuels thermal runaway reactions involving the electrolyte solvent11,12. Thus the cathode chemistries that hold greatest promise for improving LIB storage capacity, compromise cell safety by enabling uncontrollable heat release in abused cells, which is dangerously amplified in large Lithium ion battery packs with multiple cells.

There has been an upsurge in recent interest in batteries based on solid-state electrolytes that are inherently non-flammable. Wong.et.al , for example, reported that perfluoropolyether based electrolytes with a high Li+ transference number13 are simultaneously able to improve the oxidative stability of ether-based electrolytes at the high cathode potentials of interest in contemporary LIBs, and to maintain non flammability in abused cells. Other recent studies, including work by Agrawal et al. reported highly conductive, bidisperse nanoparticle hybrid electrolytes which could be formulated to exhibit low or no flammability with tunable mechanical properties14. These works are however silent about the challenges of maintaining high enough room temperature ionic conductivity in the electrolyte bulk and at the solid electrolyte interphases in the absence of a molecular solvent to facilitate ion transport.

Numerous studies have considered design rules for liquid electrolytes that preserve the beneficial transport properties of currently used electrolyte systems, but which are at the same time non-flammable. In this regard, significant efforts have been directed at developing strategies for incorporating flame retardants in liquid electrolytes15–17. Flame retardants of broadest interest function by a free radical scavenging mechanism,

which limits the number density in the vapor phase of free radical species resulting from oxidation of liquid electrolyte and thereby terminate propagation of combustion reactions induced by abuse of liquid electrolytes 18. Phosphate and halogen based compounds have emerged as particularly interesting materials because they have been proven to be effective in suppressing flammability of many of the liquids used in LIBs. Phosphates are often preferred over halogen-based materials due to their environmental benignity19. However, utilization of phosphate-based flame-retardants as electrolyte additives comes with their own drawbacks including reduced bulk and interfacial ionic conductivity in liquid electrolytes and accelerated levels of capacity fading. Efforts have been concentrated in engineering the cell components in order to prevent interference of the flame retardant with the cell performance. Among these efforts, the work by Liu et.al. stands out for its demonstration of electrospun core-shell microfiber separators that encapsulate the retardant Triphenyl Phosphate, which is released when the shell layer melts in response to a thermal trigger20. Recently, Wang et.al reported electrolytes in which a common flame-retardant, Trimethyl Phosphate, is used as the electrolyte solvent and high concentration of LiFSA/NaFSA salt used to achieve high room temperature ionic conductivity in Lithium and Sodium ion batteries21.

Here, motivated by a different design concept — namely that the large surface area available in the pores of a battery separator can be used to covalently tether desirable functional groups.22 By appropriately choosing these groups we show that it is possible to impart ion-rectification and improved safety features in liquid electrolytes. Specifically, we design and synthesize cross-linked membranes in which flame-

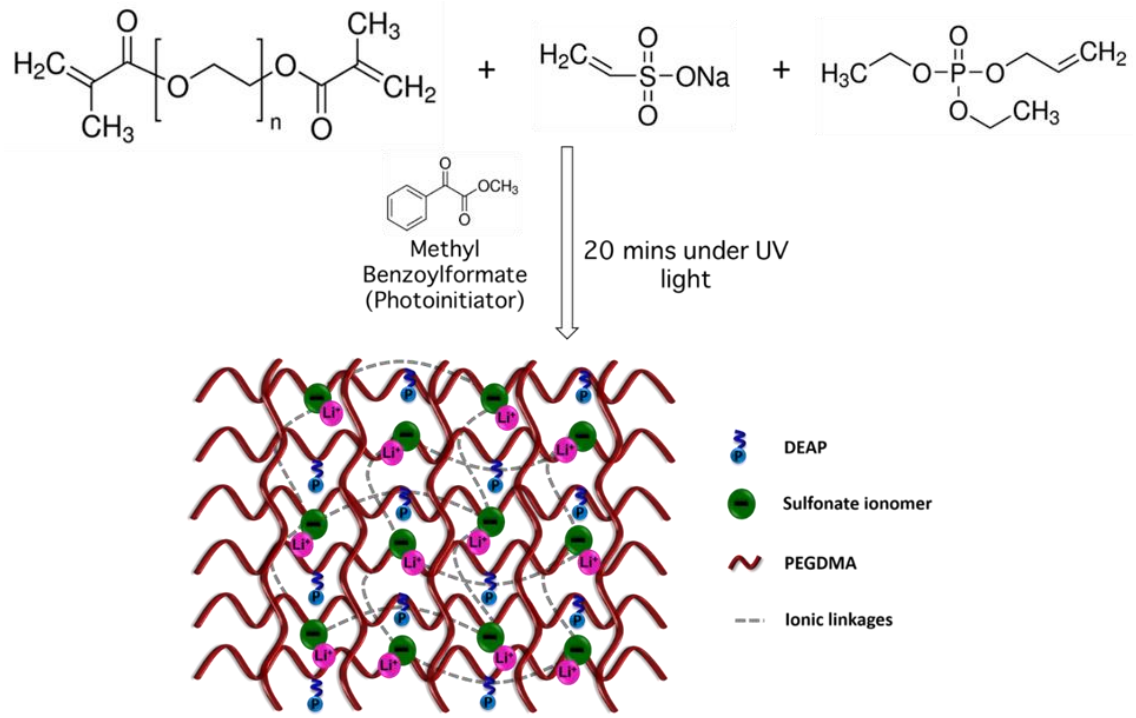
retardant molecules are covalently linked to the membrane as dangling chains. Application of the membranes as separators in LIBs is hypothesized to produce a protective "jacket" of sorts that enhances overall safety of the electrolyte. Comparison of electrolytes based on our design with those in which a similar flame-retarding agent is incorporated into the electrolyte bulk by physical mixing show that covalent tethering offers multiple benefits, including stable cell cycling, long-term flame retardancy23, and more straightforward strategies for tuning overall safety features of the electrolyte. We also investigate the effect of these pendant molecular functionalities in the cross-linked membranes on physical, chemical and thermal properties of liquid electrolytes imbibed in the membranes and show that such systems provide simple chemical routes for improving LIB electrolyte safety features without compromising other beneficial characteristics.

Results and Discussions

Scheme (1) illustrates the approach used for creating the multifunctional crosslinked membranes used in the study. Previously, we reported synthesis of cross-linked polymer membranes with pendant sulfonate ionomers and showed that when swollen with liquid electrolytes, the ionomers produce an electrostatic field throughout the electrolyte, allowing one to regulate transport and shuttling of polysulfide anions in Lithium-sulfur batteries 24. Scheme 1 shows how this approach can be extended to incorporate multiple immobilized functionalities in an electrochemical cell. By immobilizing desirable functional groups to a membrane (separator) it is possible to

largely isolate these functional groups from electrochemical processes at the electrodes, maximizing their beneficial effects in the electrolyte.

Cross-linking was achieved in solution by exposing mixtures of poly (ethylene glycol) dimethacrylate (PEGDMA), Vinylsulfonic acid sodium salt (VS), the flame retardant (Diethyl Ally Phosphate-DEAP) and the photo-initiator methyl benzoylformate (MBF) in DMSO to UV light. It is known that upon UV excitation MBF undergoes a fast bond cleavage reaction to generate free radicals able to initiate polymerization of molecules containing vinyl/acrylate groups. A unique property of PEGDMA is that upon free-radical initiation, it can make up to four covalent linkages with other molecules, which leads to spontaneous formation of cross-linked or branched molecules25. By performing the reaction in a mixture of difunctional poly (ethylene glycol) dimethacrylate (PEGDMA) and monofunctional vinylsulfonic acid sodium salt (VS) monomers we previously showed that it is possible to create cross-linked PEO networks containing covalently linked pendant sulfonate ionomer groups24. By varying the relative fractions of the di- and mono-functional monomers, the composition of dangling groups and structure of the cross-linked networks formed by PEGDMA can be facilely adjusted to create materials with a broad range of physical and mechanical properties. Here, by integrating a third monomer DEAP we show that the concept can be extended further to create networks that host multiple pendant functionalities simultaneously.



Scheme 1. Schematic diagram depicting synthesis procedure for crosslinked PEGDMA membranes with pendant sulfonate and phosphate groups. The ionic crosslinks between the sulfonate chains are also depicted

Successful cross-linking of the monofunctional and difunctional monomers was verified by X-Ray Photoelectron Spectroscopy (XPS). Prior to this and all analytical processes reported in the paper, the as prepared membranes were soaked, thoroughly rinsed in DI water, and dried. The rinsing step is an important part of the protocol as it facilitates removal of un-reacted monomer, isolated PEG and phosphate polymers not covalently linked to the network, and salt generated in the synthesis. The XPS spectra of membranes with pendant functional groups exhibit P2p and S2p peaks as shown in Fig.4.1.

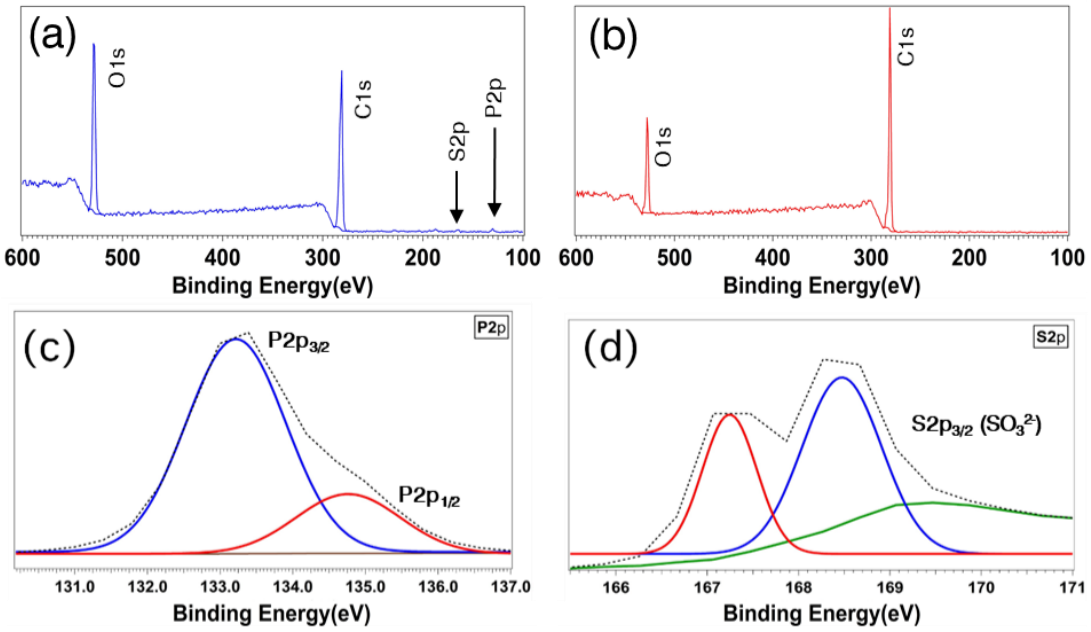


Figure 4.1. Experimental verification of crosslinking mechanism (a) XPS analysis spectrum with pendant functional groups, (b) without functional groups (c) Phosphorus 2p peaks from fitting of XPS spectrum, and (d) Sulfur 2p peaks with background (green) from Shirley fitting

As expected, these peaks are absent in the spectra of pure cross-linked PEGDMA membrane in Fig 4.1 (b). The P2p3/2 (133.2 eV) and P2p1/2 (134.6 eV) peaks in Fig 4.1(c) can be attributed to the Phosphate groups in DEAP26 and S2p3/2 peaks at 167.2eV and 168.6 eV in Fig 4.1(d) are characteristic of SO32- groups27. These results are consistent with those from complementary FTIR spectroscopic analysis reported in Fig 4.2.

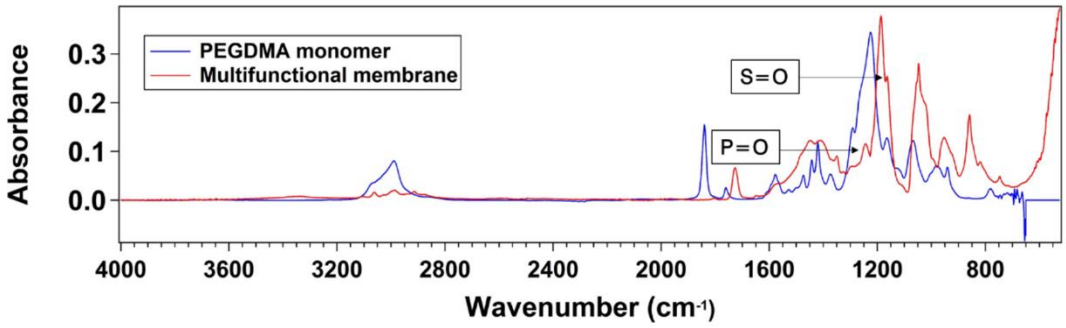


Fig 4.2 FTIR spectra of PEGDMA monomer and multifunctional cross-linked membranes synthesized using these monomers.

The morphology of the synthesized membranes as seen under the Scanning Electron Microscope (SEM) is illustrated in Fig 4.3, for the multifunctional membrane and the cross-linked analog that does not contain dangling chains. Large rope-like, intertwined polymer networks are clearly evident from the SEM micrographs for the pure cross-linked PEGDMA materials. The average thickness of the structures is large (~10µm), implying that the rope-like networks are formed from many molecules assembled together into crosslinks.

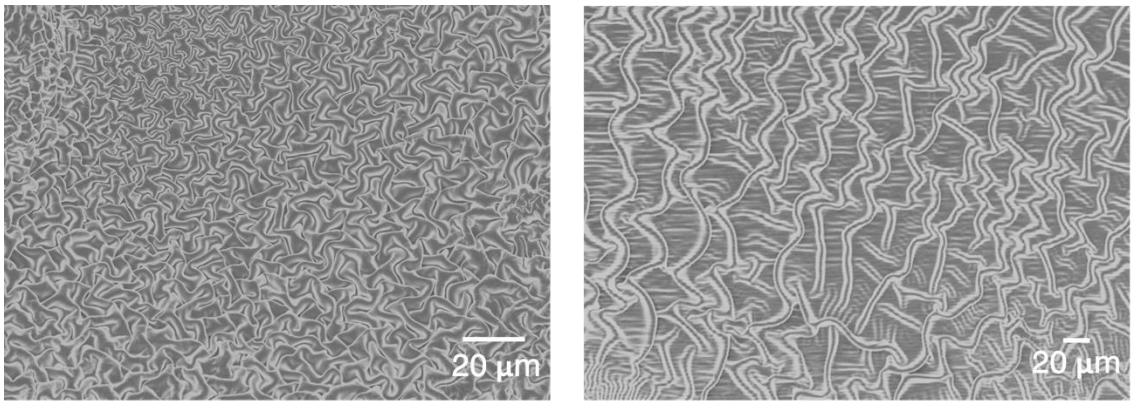


Fig 4.3 SEM images of multifunctional membrane and pure crosslinked PEGDMA membranes

An important benefit of this unusual morphological feature is that the materials are amorphous; no evidence of an amorphous to crystalline phase transition is observed in DSC analysis of the dry, bulk membranes, shown in Fig 4.4.

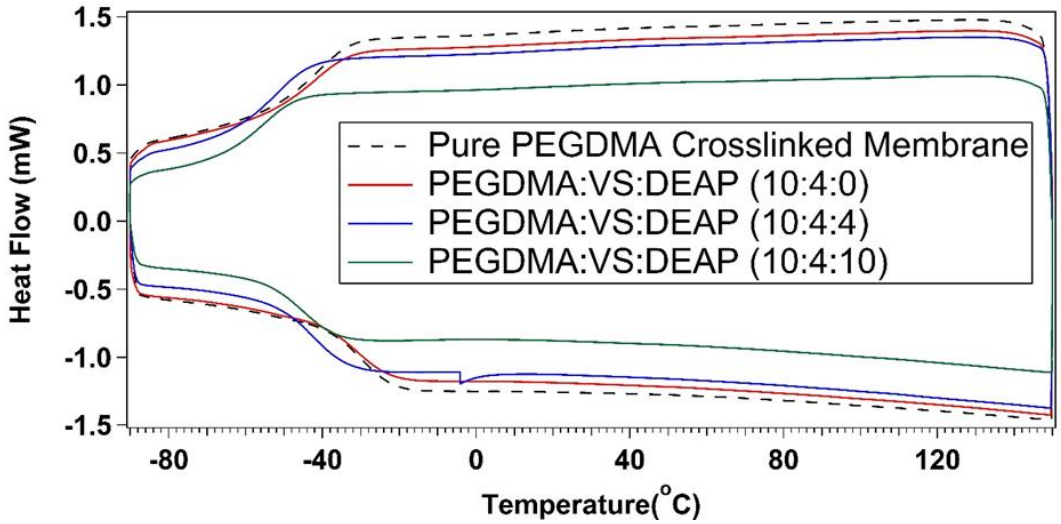


Figure 4.4 DSC analysis of dry membranes with different fractions of dangling functional groups, with mole fraction of each component in brackets

Introduction of monofunctional VS and DEAP monomers to the network is seen to reduce both the thickness and length of the rope-like structures, instead forming finer interconnected structures. This is tentatively attributed to viscosity or polymerization induced aggregation and rearrangement of PEGDMA chains as a result of ionic linkages between the sulfonate ionomers[28,29]. The uniformity and amorphous nature of the membranes proves advantageous in wettability and mechanical properties, as seen later.

The thermal properties of the multifunctional membranes and the retardant molecule DEAP were studied in detail using Thermogravimetric Analysis (TGA). Typical results are reported in Fig 4.5. The residue weight percentage in case of the multifunctional membrane matches well with the ionomer content, which forms a Li2SO4 salt residue upon thermal degradation in air. The corresponding derivative plots also provide information about the various components present on the membrane and their rate of thermal degradation compared to the monomers before crosslinking. The weight loss with increase in temperature provide information about thermal degradation of the sample. In case of DEAP, which has relatively low boiling point of 45^{o}C has maximum degradation at around 150^{o}C due to its volatility as seen from the corresponding derivative plot. This degradation peak is completely absent in case of the multifunctional membrane, whereby covalently tethering the flame retardant on the crosslinked polymer network has increased its stability against thermal degradation. In case of VS salt, it shows degradation peaks around 390^{o}C and another at 420^{o}C. This can be interpreted as an initiation reaction at the vinyl bond of the ionomer and subsequent further degradation with increasing temperature. This is also observed in

case of PEGDMA monomer, whereby there are two peaks of degradation, one at 360^{o}C and second peak at 420^{o}C. However, in case of multifunctional crosslinked membrane, there is only one degradation peak in this temperature range and this can be attributed to the fact that there are no reactive vinyl or acrylate bonds left in the membrane after crosslinking and removing unreacted monomers during synthesis. The residue weight percentage in case of the multifunctional membrane matches well with the ionomer content which forms Li_2SO_4 residue after degradation. For further studies, the previously optimized PEGDMA:VS monomer mole ratio of 10:4 was used throughout, and the DEAP content was varied to see the influence on conductivity and mechanical properties before analyzing the flame retardant properties.

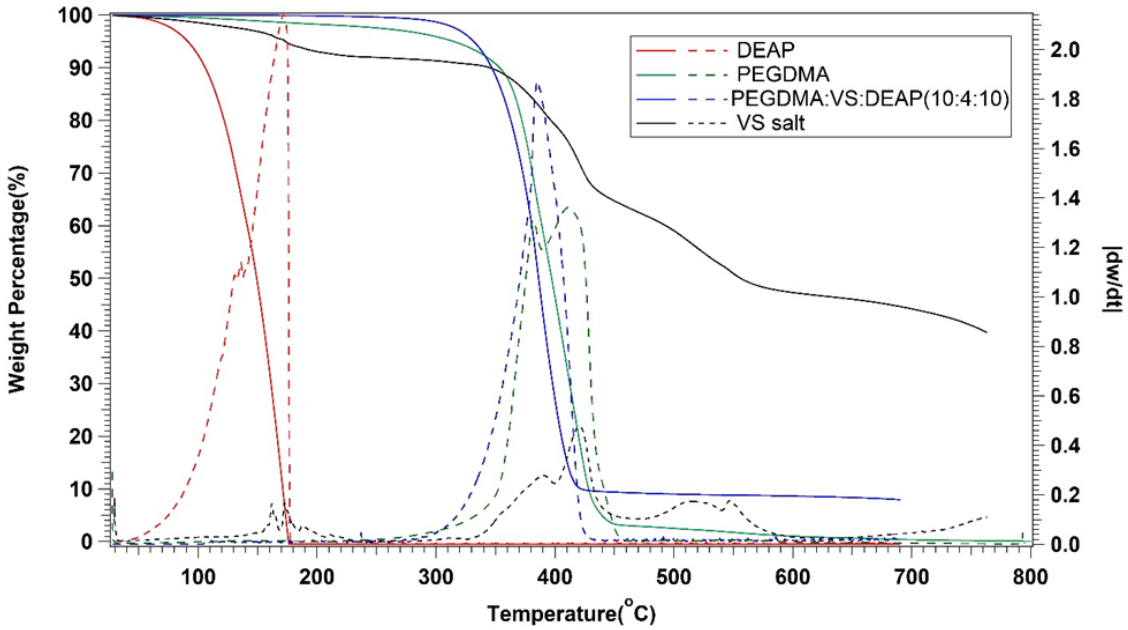


Figure 4.5 TGA characteristics of DEAP, VS salt, PEGDMA monomer and multifunctional membrane. Derivative plots (- -) show temperature of maximum degradation for each material.

The DC ionic conductivity was determined as a function of temperature for various compositions of functional groups in the multifunctional membrane after soaking in 1M LiPF6-EC/DMC (1:1) electrolyte for 24 hours. The temperature-dependent conductivity is found to be well fitted with the Vogel–Fulcher–Tammann (VFT) equation, implying that there are no melting or crystallization transitions of the soaked membranes in the temperature range tested. As seen from Fig 4.6, all membranes exhibit high conductivity values of the order~3mS/cm at room temperature and increasing the fraction of dangling chains results in increased ionic conductivity. We attribute this observation to the increased wettability of the membranes with pendant chains, whereby the nucleophilic phosphate groups and the ionic linkages between the

SO_3^{2-} ionomers increase permeability and dielectric constant of the membranes. This finding is in agreement with previously reported results, which show that pendant short branches with particular chemical properties when introduced in a cross-linked polymer network enhance CO2 permeability by increasing the local free volume available for gas dissolution and penetration[30].

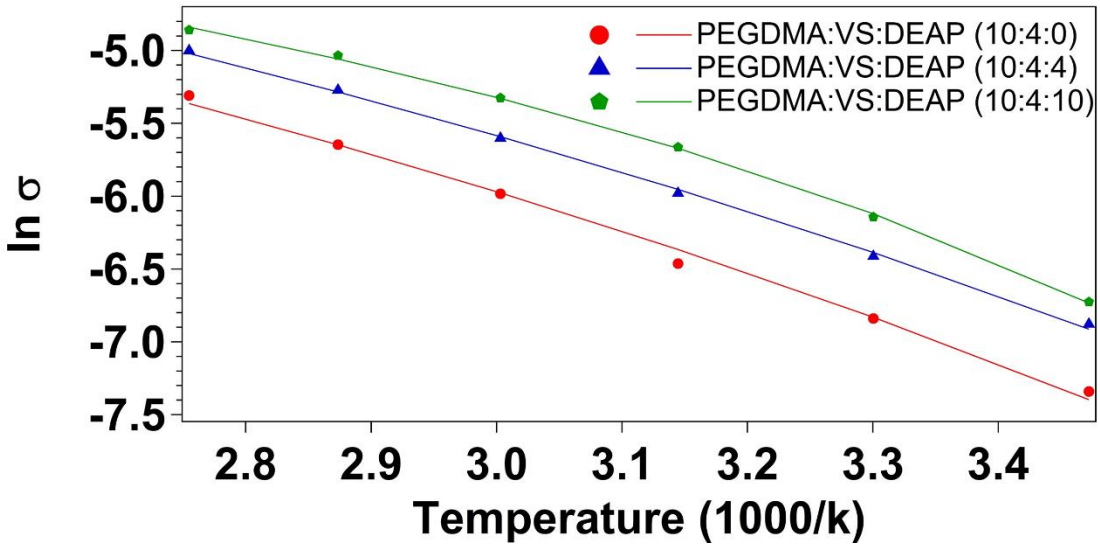


Figure 4.6 - Arrhenius plot of multifunctional membranes of different compositions

Measurements of the glass transition temperature provide a more quantitative approach for evaluating this hypothesis. When a polymer is wetted by a smaller molecular species with lower Tg, the decrease in glass transition temperature of the polymer follows a well-established dependence on the degree of plasticization[31,32]. Fig 4.7 reports the absolute glass transition temperature of different membranes and corresponding ΔTg, which is the decrease in glass transition temperature after soaking in the liquid electrolyte. As the fraction of pendant groups increase in the network, we

see that the Tg decreases and ΔTg increases, corresponding to higher electrolyte uptake.

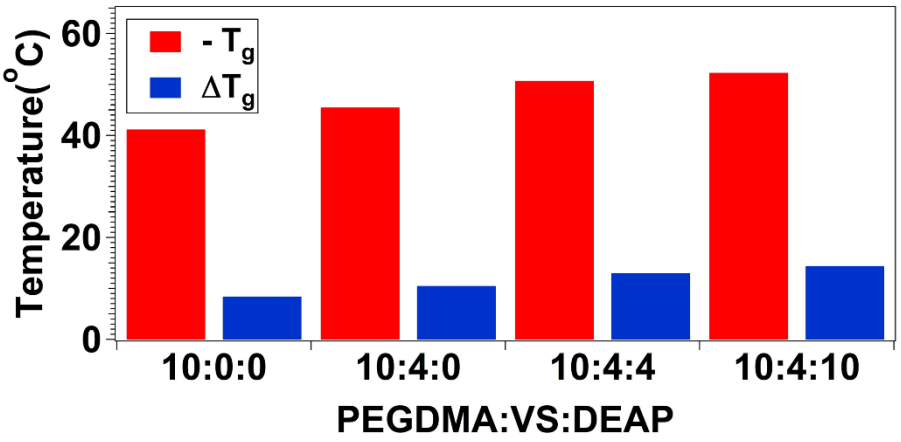


Figure 4.7 Effect of pendant functionalities on wettability and mechanical properties-Glass transition characteristics

A high storage modulus is an important requirement for a LIB separator. The storage (G') and loss modulus (G'') were determined from torsional shear analysis of the dry and solvent-swollen membranes at small strain amplitude (γ = 0.1%) (Fig 3.8). It is seen that in all cases the dynamic storage modulus G' is more than an order of magnitude larger than the dynamic loss G" modulus and nearly independent of frequency, indicating that the materials are solid-like whether swollen or not swollen by solvent. It is also apparent that the storage modulus for the pure crosslinked PEGDMA membrane is high (60 MPa) and the introduction of pendant groups lower the modulus. This is consistent with our previous statement that pendant chains in the network increases available local free volume. However, we also believe that the

resilience of the mechanical properties in networks made more defective by incorporation of pendant groups reflects a partial compensation of elasticity by ionic cross-links induced by the sulfonate ionomers. Soaking the membranes in liquid electrolytes results in an additional factor of 3 reduction in modulus, but even then the elastic modulus of the materials (5MPa) is still high-enough to function as a LIB separator. On that basis, we conclude that a mole ratio of 10:4:10 (PEGDMA:VS: DEAP) is optimal with respect to ionic conductivity and storage modulus.

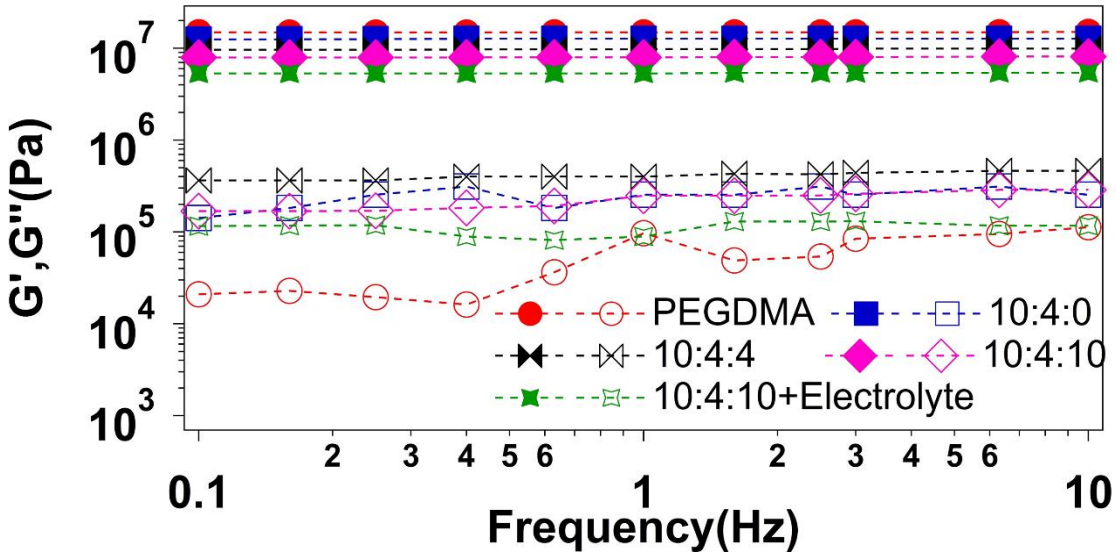


Fig 4.8 Storage and Loss modulus as a function of frequency

In order to understand how the pendant chains impact safety characteristics and electrochemical performance of batteries, we compared flame retardance and electrochemical properties of the electrolyte-swollen membranes with those of electrolytes in which the same flame retardant is used as an additive. There is already a large body of work on how flame retardant additives adversely impact

electrochemical performance of LIBs [33,17,34,35]. For convenience, we first studied DEAP as the flame retardant additive for 1M LiPF6 in EC/DMC. The flame retarding mechanism is believed to be due to a free-radical scavenging reaction, whereby DEAP releases PO● and PO2● which capture H● and OH● radicals from burning of the electrolyte in the vapor phase and terminate the chain reaction that produces combustion36. The self-extinguishing time measured for electrolytes with different amounts of DEAP are reported in Fig 4.9.

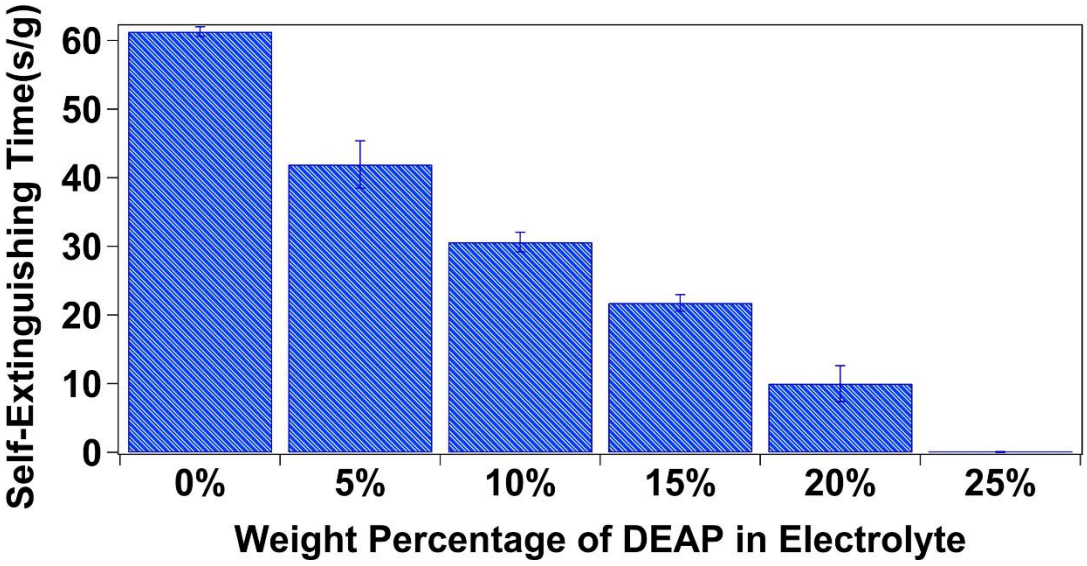


Figure 4.9 Physical incorporation of flame retardants in liquid electrolytes-Self Extinguishing time of electrolytes with different fractions of DEAP in 1M LiPF6 in EC/DMC

To perform these measurements, glass fiber mats were soaked in each electrolyte for a preset time and the mass change recorded. Following the soaking period, mats were removed and ignited using a butane torch held at a fixed distance from the mat. The

time required for the initial flame to burn out divided by the mass of electrolyte taken-up by the mat defines the self-extinguishing time for the electrolyte. As expected, the time to self-extinguish decreases with increasing DEAP content and the electrolyte is considered non-flammable when 25 wt% or more DEAP is added. The Arrhenius plot for the various compositions is shown in Fig 4.10.

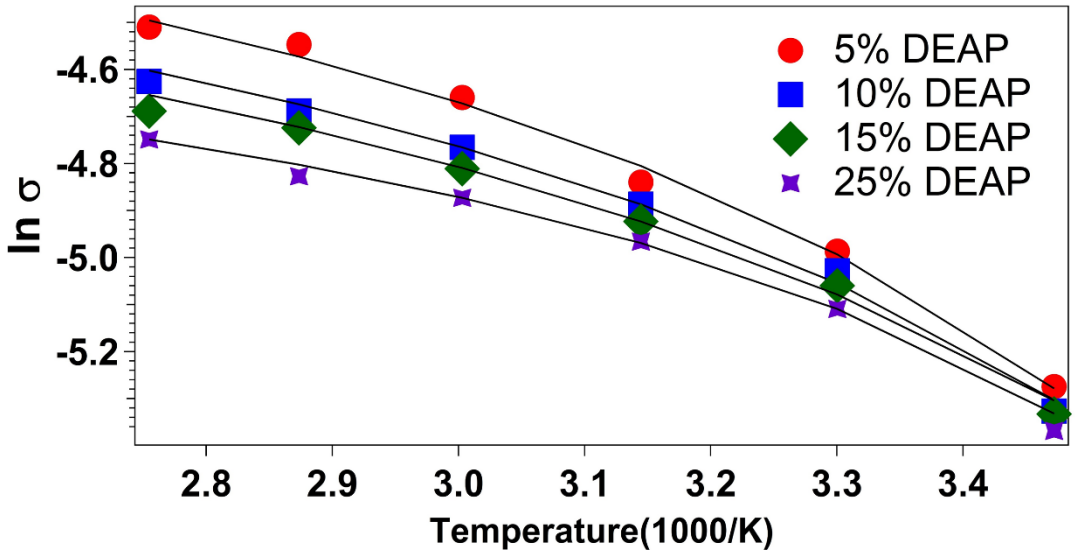


Figure 4.10 Physical incorporation of flame retardants in liquid electrolytes-Arrhenius plot depicting decreasing DC ionic conductivity with increasing flame retardant concentration

Increase in DEAP content leads to decrease in conductivity, though the decrease is still within the acceptable range of conductivity values for Lithium ion battery electrolytes. Electrochemical analysis of the electrolytes were performed using

$LiFePO_4$/Graphite full cells. In these cells 100µL of 1M $LiPF_6$ in EC/DMC (50/50 v/v) with 25 wt % of DEAP was used as electrolyte and commercial Celgard 3501 was used as the separator and the cells were subjected to galvanostatic cycling at a fixed rate of C/3. The voltage profiles reported in Fig 4.11 shows large changes from as early as the 2nd cycle and continues degradation of storage capacity in subsequent cycles.

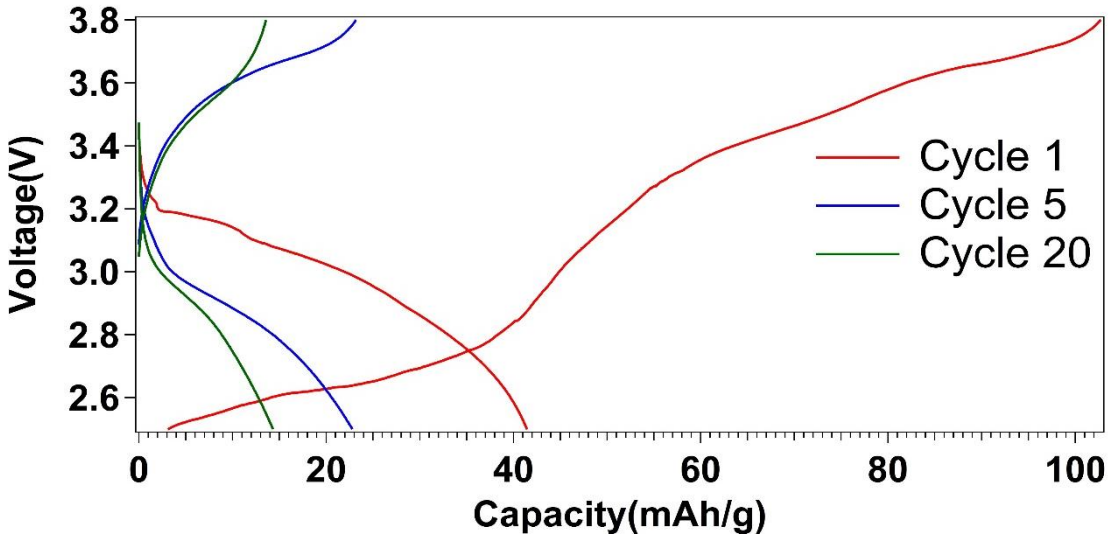


Figure 4.11 Physical incorporation of flame retardants in liquid electrolytes-Voltage Profiles of electrolyte with 25% DEAP in a LiFePO4/Graphite full cell

A conventional explanation for this observation is that the flame-retardant additive leads to formation of mechanically poor interfaces at the LIB anode where DEAP is subject to continuous reduction. To confirm this, impedance measurements were performed in a symmetric Li/Li cell to study the interfacial transport behavior of DEAP near a highly reducing electrode. Fig 4.12 shows the Nyquist plots for various

compositions of DEAP in the electrolyte. It is clear from these results that the interfacial resistance increases with increasing DEAP content.

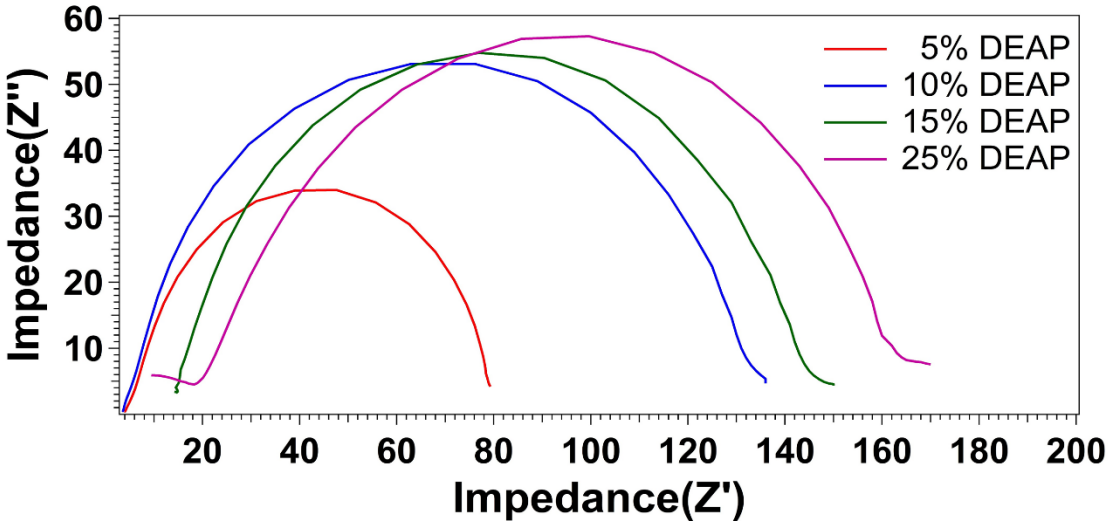


Figure 4.12-Nyquist plots for different compositions of DEAP in electrolyte

Figure 4.13 further reports the evolution of impedance during strip-plate test of 25% DEAP in 1 M LiPF6 in EC/DMC in a symmetric Li/Li coin cell. Increasing impedance with each cycle further confirms the unfavorable interface formed due to reaction with lithium.

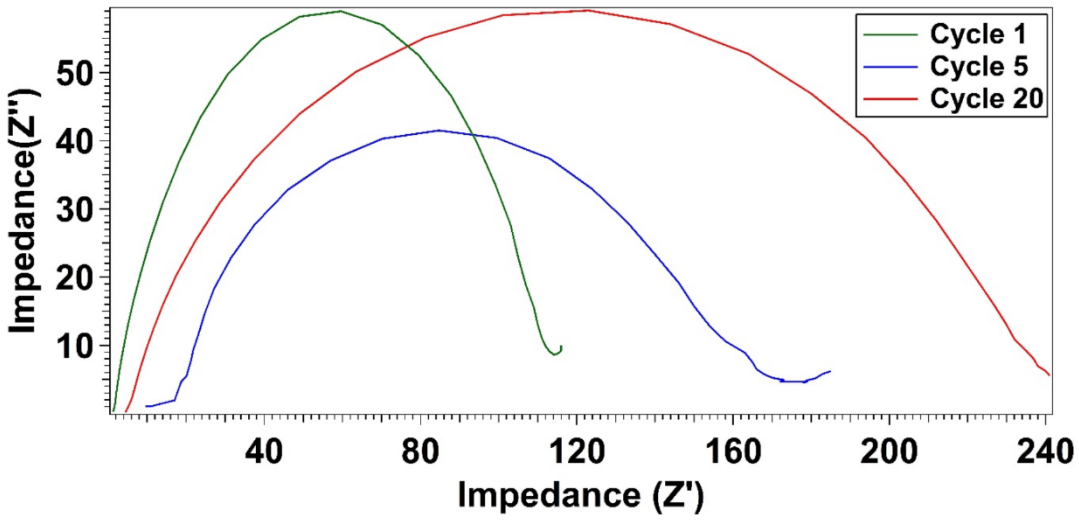


Figure 4.13 Evolution of interfacial impedance during strip-plate test of 25% DEAP in 1M LiPF6 in EC/DMC in a symmetric Li/Li coin cell. A current density of 0.2 mA/cm2 was used.

Having confirmed the disadvantages of improving safety by using the flame retardants as additives in a liquid electrolyte, we studied how immobilizing the flame retardant on the separator renders it non-flammable without compromise on the electrochemical performance. Fig 4.14 reports the electrochemical stability window for the soaked multifunctional membranes with different compositions obtained from linear sweep voltammetry.

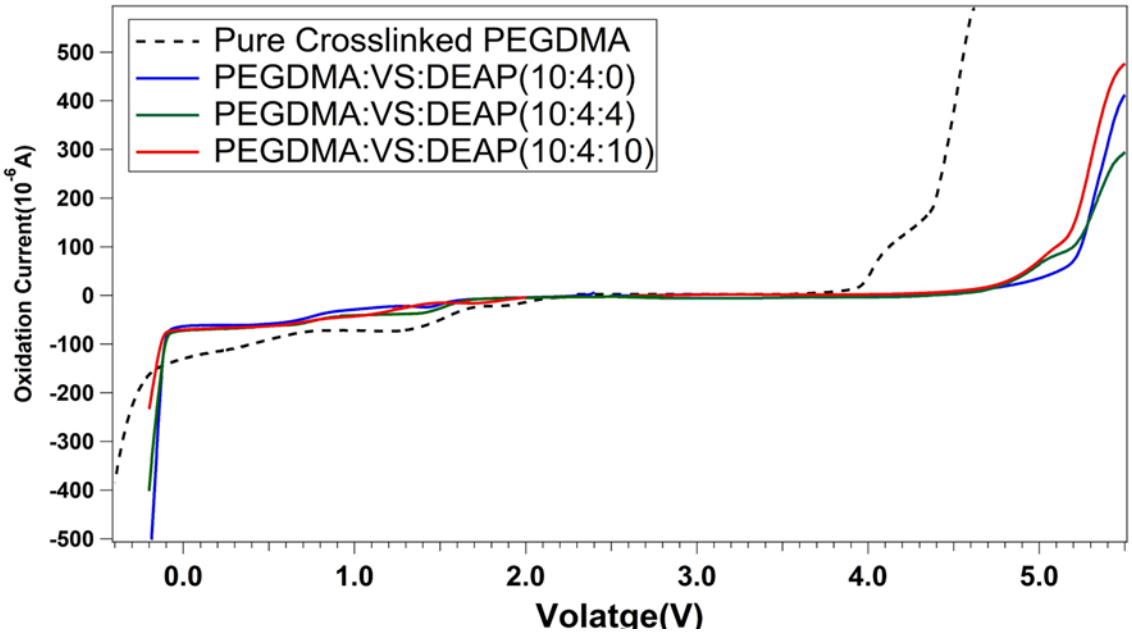


Figure 4.14. Cyclic Voltammetry results of soaked multifunctional membranes with Pure PEGDMA crosslinked membrane as reference with a scan rate of 10mV/s

It is well known that PEO breaks down close to 4V[37] and this is seen from the onset of oxidation at~4V for crosslinked PEGDMA. The oxidation stability is seen to increase, by at least 1 V (Stability Window of the electrolytes increases from approximately 4V to 5V) in case of the multifunctional membranes. We attribute this result to rectification of anion transport by the negative charges imparted by the sulfonate ionomers to the membranes. Our previous results show that whether such charges are present in a bulk membrane in the inter-electrode space[24] or as a nanometer thin interfacial phase coated on the separator[38] or electrode,[39-40] they are highly effective in rectifying transport of negatively charged species in liquid electrolytes. Here we believe that the charged membranes serve to simultaneously limit access of anions to the highly oxidizing electrode surface and to constrain oxidation products from the

PEO degradation to a self-limiting region near the electrode, limiting wholesale, bulk decomposition of the PEO electrolyte.

Impedance spectroscopy was utilized to study the interfacial behavior in a symmetric cell with lithium as the two non-blocking electrodes. The Nyquist plots for the multifunctional membranes are shown in Fig. 3.15. Results are consistent with DC ionic conductivity measurements, whereby increasing the fraction of pendant groups results in reduced bulk as well as interfacial impedance.

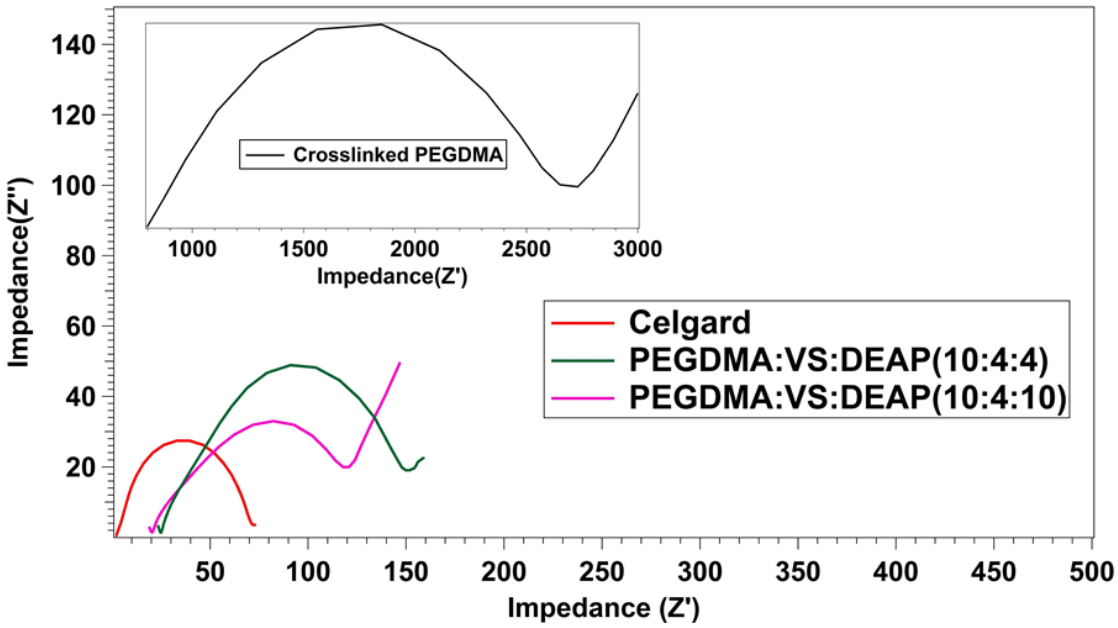


Figure 4.15 Nyquist plots for different membranes and commercial Celgard seperator soaked in electrolyte

The inset figure shows impedance data for pure PEGDMA crosslinked membrane soaked in electrolyte and the high bulk and interfacial impedance is a result of the poor wettability and electrolyte uptake of the membrane without any pendant groups. When directly compared to the impedance of the electrolyte with DEAP as an additive, we see that the multifunctional membranes have a more favorable interface with lithium, due to the prevention of reduction of the fire retardant on lithium.

To evaluate the application of the multifunctional membranes as electrolyte/separator in a lithium ion battery, LiFePO4-Graphite full cells were constructed with membranes soaked in 1M LiPF6 in EC/DMC electrolyte without any additives. Fig. 4.16 shows the cycling data at a rate of C/3 for the multifunctional membrane electrolyte as well as DEAP physically mixed in electrolyte for comparison.

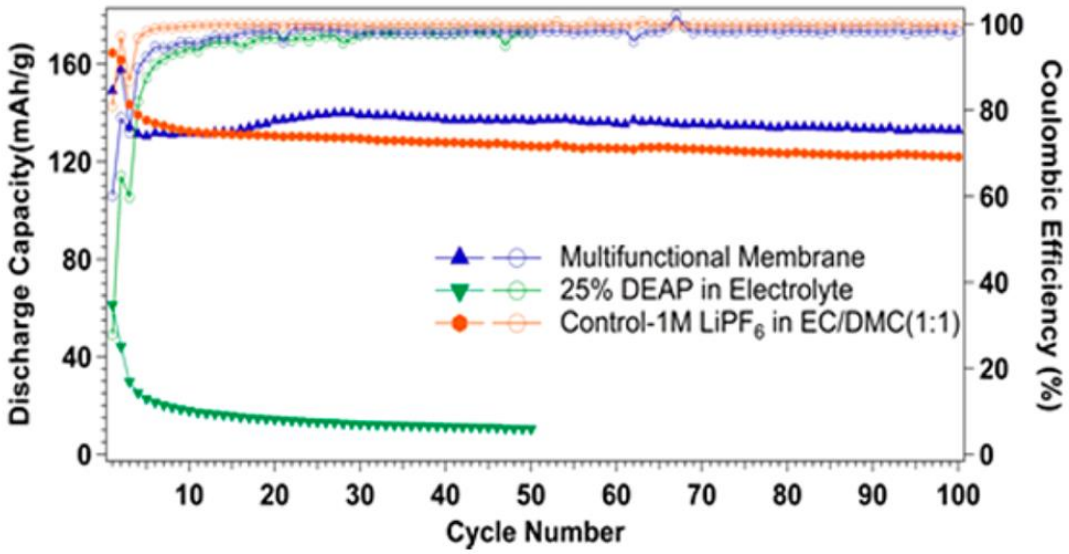


Fig 4.16 Discharge Capacity and Coulombic Efficiency of full cell with soaked multifunctional membrane and electrolyte with DEAP additive for 100 cycles

The multifunctional membrane proved stable without any additives in the full cell, cycling stably for 100 cycles with >99% coulombic efficiency. This is in stark contrast compared to the electrolyte with physically mixed DEAP, whereby, as seen earlier, the irreversible capacity loss from the 1st cycle is evident with only 25% capacity retention in the first charge-discharge cycle. This further proves the stability of the flame retardant when immobilized on the separator, whereby it is no longer able to participate in side reactions with the graphite anode and interfere with ion transport at the interface. The stable voltage profiles (4.17) show relatively low overpotential at a rate of C/3 for each cycle, and this can be attributed to good wettability of the membrane and it's single-ion conducting nature.

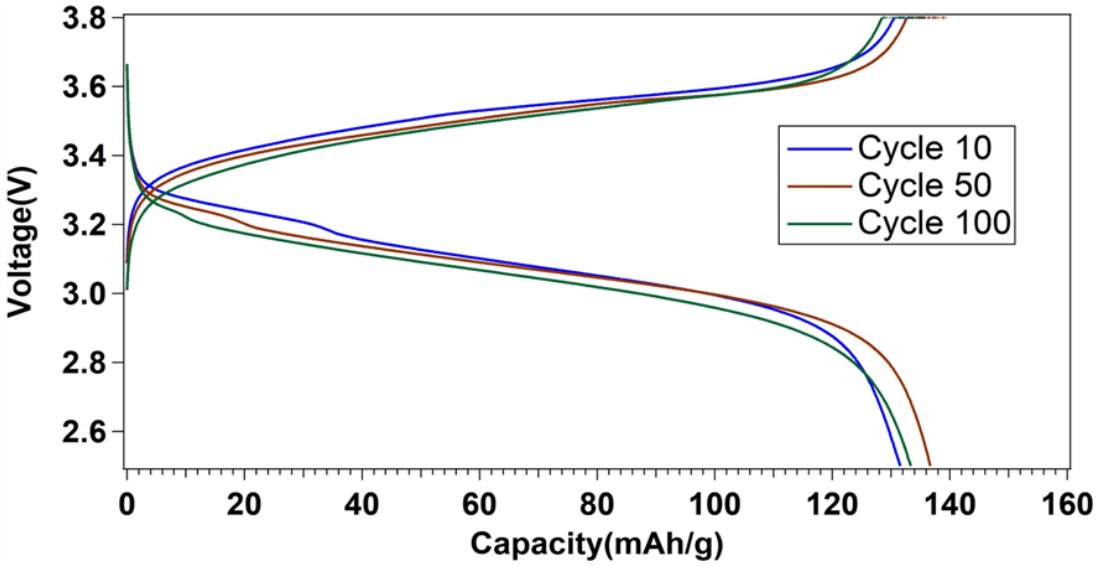


Fig 4.17 Voltage profiles for different cycles in a LiFePO4/Graphite full cell with multifunctional membrane (PEGDMA:VS:DEAP-10:4:10) soaked in electrolyte

The high voltage stability of the multifunctional membrane electrolyte was evaluated with a commercial high voltage cathode, in this case, LCO. Full cells with LCO as the cathode and graphite as the anode were assembled with the multifunctional membrane and Celgard in the control case for comparison, after soaking in electrolyte for 24 hours. Cycling data and voltage profiles(inset) are reported in Fig. 4.18 for a cycling rate of C/3 over 50 cycles.

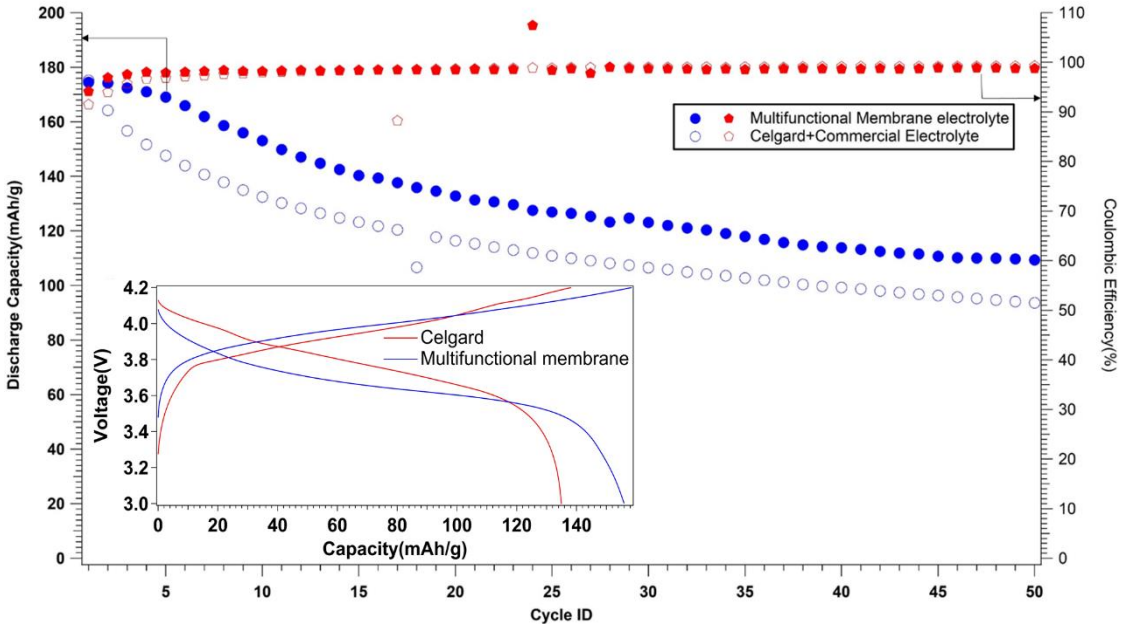


Figure 4.18. Discharge Capacity and Coulombic efficiency for multifunctional membrane electrolyte and Commercial Celgard soaked in electrolyte in LCO-Graphite full cells, (inset)Voltage profiles for charge-discharge cycle for Celgard+electrolyte (red) and multifunctional membrane electrolyte(blue)

Comparable performance to Celgard is achieved in case of multifunctional membrane. The overpotential is seen to be slightly higher compared to the control case and this may be due to the higher interfacial resistance in case of the membrane compared to Celgard as seen previously. This can be better controlled by reducing the thickness of the membrane to values comparable to the standard Celgard membrane used in Lithium-ion cells.

Finally, the thermal stability of the membranes soaked in electrolyte was analyzed by measuring the self-extinguishing times using the same flame testing process detailed earlier. All separators were soaked in 1M LiPF6 EC/DMC electrolyte prior to test. As seen from Fig.4.19, Celgard with electrolyte combusts on ignition and is destroyed in merely few seconds. Though cross-linked PEGDMA proves to be less readily combustible compared to Celgard, it still catches fire due to the flammability of the electrolyte and its intrinsic tendency to combust at elevated temperatures. The multifunctional membrane on the other hand is observed to be non-flammable due to the large number of pendant phosphate chains incorporated in the membranes, which suppress electrolyte combustion. This concept can also be applied to create flame-retardant membranes based on commonly used commercial polypropylene separators by first coating it with the precursor material and initiating the crosslinking reaction. As shown in Fig. 4.19 (d) separators infused with crosslinked membrane at the optimal composition are non-flammable.

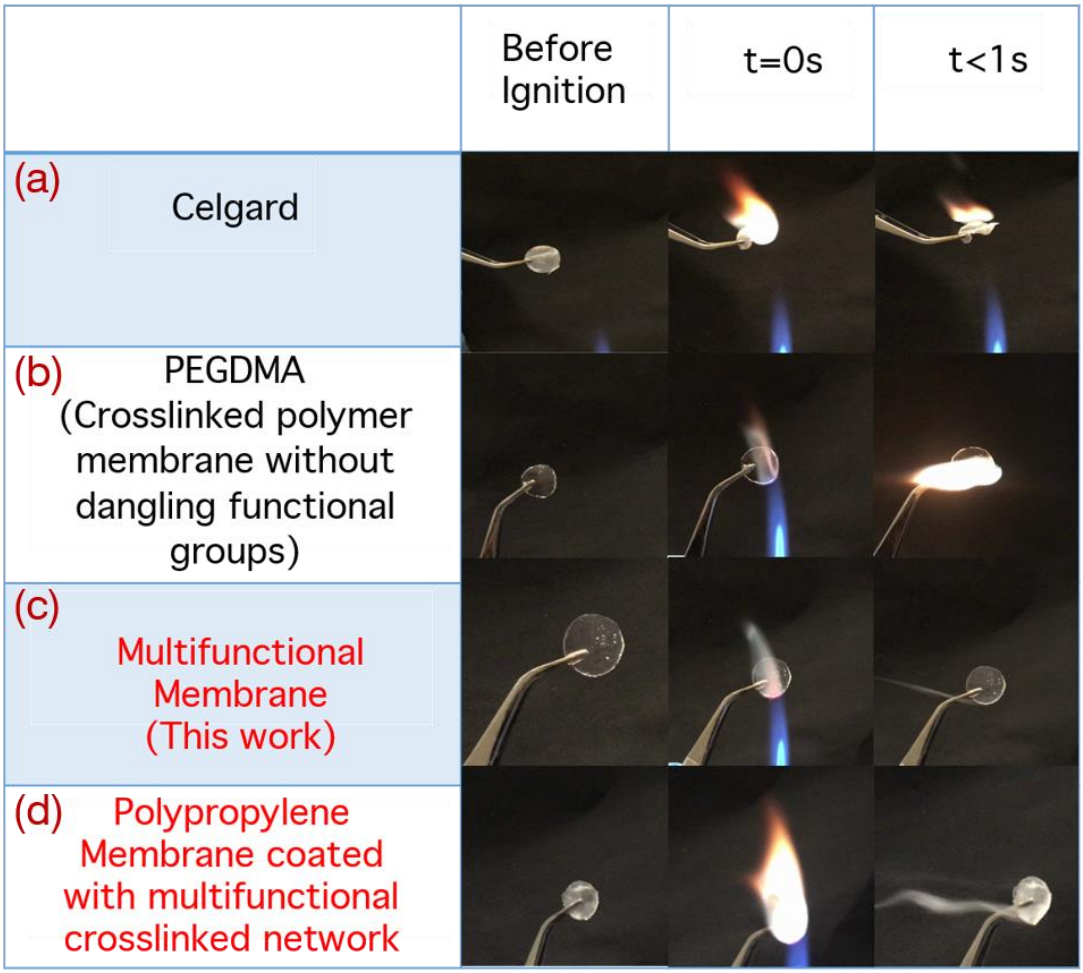


Fig 4.19 Flame retardant properties of soaked multifunctional membranes compared to commercial seperator (a) Celgard, (b) Pure crosslinked PEGDMA, (c) Multifunctional membrane and (d) Multifunctional membrane as a coating on commercial separator

Conclusions

In conclusion, we report a facile route to prepare cross-linked multifunctional membranes with multiple pendant functionalities to improve safety and electrochemical performance of LIB electrolytes, simultaneously. The physical and mechanical properties of the membranes are studied and found to be easily tuned by changing the fraction of pendant chains employed in the synthesis. By means of self-extinguishing flame studies and electrochemical analysis, the membranes are shown to be highly efficient in improving safety characteristics of LIB electrolytes, while at the same time overcoming the well-known problem of interference of fire retardant additives with cell performance. As a final demonstration, we show that the same chemistry employed to create optimal free-standing membranes can be used to incorporate flame retardancy to a conventional polyolefin separator by using it as a support for the cross-linking reaction of the membrane components.

Materials and Methods

Membrane preparation: Multifunctional membranes were prepared using a scheme similar to previously reported. PEGDMA(Mw=750) and Vinylsulfonic acid sodium salt solution (25 wt% in H2O) and Diethyl Ally phosphate (DEAP) were purchased from Sigma Aldrich. VS salt was dried in vacuum oven for 24 hours and dissolved in DMSO (25 wt%). PEGDMA and DEAP were added to the DMSO solution in the desired molar ratio and stirred till a uniform solution was obtained. 5% Methyl benzoylformate (Sigma Aldrich) photoinitiator was added to the solution and the solution was cast on a Teflon plate for crosslinking under UV light (VMR UVAC 115 V ~60 Hz 254/365 nm) for 20 minutes. Membranes of 100μm were harvested and

washed with DI water to remove the DMSO and unreacted monomers. The membranes were then kept in a 3M LiOH solution for ion-exchange between Na+ and Li+. After 24 hours the membranes were washed with DI water and kept under vacuum for 24 hours at 80oC to remove excess water. The membranes were then punched out and stored in an Argon-glovebox before use.

Characterization: The membranes were characterized by X-ray Photoelectron Spectroscopy using Surface Science Instruments SSX-100 with operating pressure of ~2×10-9 torr. Monochromatic Al K-α x-rays (1486.6eV) with beam diameter of 1mm were used. Photoelectrons were collected at an emission angle of 55° and the electron kinetic energy was determined by a hemispherical analyzer, where a pass energy of 150V was used for wide survey scans and 50V for high resolution scans. CasaXPS software was used for XPS data analysis with Shelby backgrounds and the spectra were referenced to adventitious C 1s at 284.5 eV. Morphologies of the membranes were studied using a LEO 1550 FESEM (Keck SEM). Mechanical properties of the membranes were investigated by dynamic mechanical analysis (DMA) using a TA Instruments DMA Q800. Thermogravimetric analysis (TGA) was used to determine the thermal degradation of different compositions of the membranes. Impedance versus frequency was measured using a Novocontrol N40 broadband dielectric spectroscopy instrument. Ionic conductivity as a function of frequency was also measured with a Novocontrol N40 broadband spectrometer fitted with a Quarto temperature control system. The samples were swelled in the electrolyte for 24 hours in the glovebox. The swollen membranes were punched into ½ inch diameter discs and sandwiched between stainless steel plates for conductivity measurements. Self-

extinguishing time measurements were done by igniting the membranes/separators of interest, after soaking in electrolyte, using a butane torch at a fixed distance. The time to self-extinguish was measured and normalized using the mass of the soaked material. Electrochemical Characterization: 2030 coin-type cells were assembled in a glovebox (MBraun Labmaster) using LiFePO4 (2mAh/cm2, MTI corp.) or LCO (NOHMS Technologies) as the cathode and Graphite (NOHMS Technologies) as the anode. The loading on the electrode materials were 2mAh/cm2. The prepared membranes swollen with 1M LiPF6 in EC/DMC(50/50 v/v) served as the separator/electrolyte and Celgard 3501 was used in the control case. The room-temperature cycling characteristics of the cells were evaluated under galvanostatic conditions using Neware CT-3008 battery testers, and electrochemical processes in the cells were studied by linear sweep voltammetry using a CHI600D potentiostat.

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